

Pace-Argentine



374990

**U.S. Environmental Protection Agency Region VIII
Field Sampling Plan
Case Number _____**

Mercury TMDL Development
McPhee, Narraguinne, and Sanchez Reservoirs, Colorado

Anticipated Sampling Dates: June and August, 1999
Fish Sampling in May 1999

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Based on Field Sampling Plan for Two Lakes in Arizona
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1.0 INTRODUCTION AND OBJECTIVES

Introduction

Based on high levels of mercury in fish tissue samples, Colorado has listed Sanchez and McPhee Reservoirs as water quality-limited waters pursuant to section 303(d) of the Clean Water Act (CWA). Narraguinnep Reservoir is currently fed by outflow from McPhee Reservoir and also has elevated mercury concentrations in fish tissue.

In June and again in August 1999, field water, macroinvertebrates, and sediment sampling of Sanchez, McPhee, and Narraguinnep Reservoirs and selected tributaries will be conducted to quantify potential sources of mercury and to support the estimation of mercury total maximum daily loads (TMDLs). Fish sampling will be conducted in October 1999. The TMDL process is specified in the Clean Water Act (CWA) for addressing impairment in water quality-limited waters in which technology-based controls of point sources are not sufficient to achieve designated uses. The TMDL is specified as the sum of wasteload allocations (for point sources), load allocations (for nonpoint sources), and a margin of safety. For these reservoirs, load allocations and the margin of safety are relevant. Load allocations could include natural background, seepage and sediments from waste piles and tailings from historic mining operations, atmospheric deposition, agricultural return flows, eroded soils due to grazing and timber operations, natural and anthropogenic mercury releases associated with oil and gas operations, and recycling of mercury from sediments in the reservoirs. Ponds with treated effluent from a sewage treatment plant may impact the Dolores River prior to its discharge into McPhee Reservoir during flooding. However, this is not thought to be a primary source for mercury. Another factor is that McPhee Reservoir is a relatively new reservoir that finished filling in 1986. New reservoirs are known to have higher mercury loadings for 20 to 30 years after completion due to flooding of vegetation and soils, increased availability and decay of organic matter, and other factors (Bodaly, 1984, Brouard et al, 1990; Rosenberg et al, 1997). Many of the available fish samples were collected three to five years after its completion. Because of the extensive gold mining operations that have occurred in the Dolores River basin and results of available sampling data, the reservoir effect is not thought to be solely responsible for the observed high fish mercury concentrations in McPhee Reservoir. Narraguinnep Reservoir is an old reservoir, built in 1907, and enlarged in 1956. Prior to 1986, this reservoir's inflow came from a tunnel from the Dolores River. In 1986, the inflow was changed to outflow from McPhee Reservoir at Great Cut Dike.

Ultra-clean water sampling will be conducted by trained staff from Frontier Geosciences in Seattle, Washington under the direction of Nicolas Bloom, one of the developers of these methods. Sediment and macroinvertebrate sampling will be conducted by Frontier and Tetra Tech staff. Fish sampling will be conducted by the US Fish and Wildlife Service (USFWS) and the Colorado Department of Wildlife (CDOW). The procedures for fish sampling and analyses to be used are included in the appendix.

A EPA approved Lab will perform TOC, grain size, sulfate, and sulfide analyses on sediment samples, and major cations and anions, alkalinity, total dissolved solids (TDS), and dissolved organic carbon (DOC) on water samples. TetraTech will perform analyses for total suspended solids (TSS) and chlorophyll *a* in the water samples. A Class 100 laboratory will perform the total mercury (Hg) and methyl mercury (MeHg) analyses on the water, sediment, and macroinvertebrate samples. Total mercury analyses on the fish tissue samples will be performed by the CDOW laboratory. Class 100 Labs will perform total mercury analyses on splits of at least 10 percent of the fish tissue samples.

McPhee Reservoir Objectives

The overall objective of the McPhee Reservoir sampling effort is to support the development of a mercury TMDL by quantifying mercury sources to the reservoir and by understanding the mercury cycling within the reservoir. Quantification of the dissolved and total aqueous mercury concentrations in McPhee Reservoir will help quantify the load to Narraguinnep and Totten Reservoirs, both of which receive outflow from McPhee. Specific objectives include 1) the characterization of selected mining discharges that could impact tributaries to the Dolores or West Dolores Rivers and hence McPhee Reservoir, 2) the characterization of mercury in water column, macroinvertebrates, and sediments from the Dolores River where it discharges to McPhee, 3) the characterization of the water column and sediments at the treatment ponds at the town of Dolores, 4) determine if runoff from nearby oil/gas exploration or operations could impact the reservoir, and 5) the characterization of the reservoir sediments, macroinvertebrates, and water quality. Fish will be collected in the reservoir. Along with assisting the TMDL project described in this plan, coordination with the US Fish and Wildlife Service (USFWS), the Colorado Dept. of Wildlife (CDOW) and the Colorado Dept. of Public Health and Environment (CDPHE) Water Quality Control Division should assist the state's monitoring program and the CDOW fish advisory program.

Previous water quality and sediment sampling conducted in the Dolores River basin in the 1950's and 60's showed that water quality and aquatic biota of the upper reaches of this river, notably above the confluence with Silver Creek, were impacted by gold/silver and other types of hard rock mining. Recent water quality sampling was conducted by the US Bureau of Reclamation (USBR) and the US Geological Survey (USGS) in 1989 and 1992; sediment sampling was performed in 1989 and 1993. Water and sediment samples from McPhee Reservoir and selected tributaries were collected in 1994 as part of the EPA's routine screening under CERCLA. Fish sampling in McPhee Reservoir was conducted by USBR in 1988; CDOW in 1989, 1991, and 1993; and by USFWS in 1990; and in the Dolores River in 1989 by the USBR. Elevated fish mercury concentrations were found in some predator fish samples. Macroinvertebrates, plants, and algae in the reservoir and selected tributaries in the irrigated areas were collected and analyzed for mercury by the USGS in 1989 and 1990. The Rico Mining District is located in the upper part of the Dolores River Basin, and mercury has been detected in mine wastes and seepage in this area, and in water and sediment samples from several tributaries and the Dolores River. The Bear Creek watershed, a tributary to the Dolores River, has copper deposits of the La Plata

Mining District, and has had mining operations. Historically, placer mining for gold has occurred in the La Plata District, which could result in impacts where the mercury amalgamation process was used. This sampling event in the summer of 1999 should identify the mine discharges that are a significant source of mercury loading to the reservoir, and determine whether mercury is present in other tributaries, the main-stem Dolores River, or the West Dolores River. No ultra-clean sampling for mercury of the reservoir or tributaries has been conducted previously. The new sampling data will also determine if there are other significant anthropogenic sources to the reservoir. This sampling trip will provide data needed to characterize methylation rates in the reservoir and the distribution of mercury in the reservoir and tributary sediments.

Narraguinnep Reservoir Objectives

The overall objective of the Narraguinnep Reservoir sampling effort is to support the development of a mercury TMDL by quantifying mercury sources to the reservoir and by understanding the mercury cycling within the reservoir. The dissolved and total aqueous mercury concentrations in the inflow from McPhee Reservoir will be quantified. Narraguinnep was supplied by a tunnel from the Dolores River from 1907 until 1986, when the inflow was changed to outflow from McPhee Reservoir. As discussed above, the Dolores River has been impacted by recent and historical gold/silver mining. Specific objectives include 1) the characterization of agricultural discharges to the reservoir, 2) the characterization of mercury in water column and sediments in the tributaries to the reservoir, 3) determine if past mining discharges have resulted in elevated mercury concentrations in sediments, 4) determine if runoff from nearby oil/gas exploration or operations could impact the reservoir, 5) determine if any wetland areas exist along the reservoir and if so, determine if mercury is present, and 6) the characterization of the reservoir sediments, macroinvertebrates, and water quality. Fish will be collected in the reservoir. Along with assisting the TMDL project described in this plan, coordination with the US Fish and Wildlife Service (USFWS), the Colorado Dept. of Wildlife (CDOW) and the Colorado Dept. of Public Health and Environment (CDPHE) Water Quality Control Division should assist the state's monitoring program and the CDOW fish advisory program.

Previous water quality and sediment sampling conducted in the Dolores River basin in the 1950's and 60's showed that water quality and aquatic biota of the upper reaches of this river, notably above the confluence with Silver Creek, were impacted by gold/silver and other types of hard rock mining. Recent water quality sampling was conducted by the US Bureau of Reclamation (USBR) and the US Geological Survey (USGS) in 1989 and 1992; sediment sampling was performed in 1989 and 1993. The Rico Mining District is located in the upper part of the Dolores River Basin, and mercury has been detected in mine wastes and seepage in this area, and in water and sediment samples from several tributaries and the Dolores River. The Bear Creek watershed, a tributary to the Dolores River, has copper deposits of the La Plata Mining District, and has had mining operations. Historically, placer mining for gold has occurred in the La Plata District, which could result in impacts where the mercury amalgamation process was used.

Water quality sampling in Narraguinnep Reservoir was conducted by the US Geological Survey (USGS) in 1977 and 1980 and for routine screening under CERCLA by EPA in 1994; soil and sediment sampling was conducted by the USGS in 1990 and sediment only by EPA in 1994. Fish sampling in Narraguinnep Reservoir was conducted by CDOW in 1989. Elevated fish mercury concentrations were found in some predator fish samples. This sampling event in the summer of 1999 should characterize the agricultural discharges and determine if they are a source of mercury to the reservoir, determine whether elevated mercury concentrations from past mining discharges are present in sediments, and determine whether mercury is present in the inflow from McPhee. No ultra-clean sampling for mercury in the reservoir or tributaries has been conducted previously. This sampling trip should also provide data needed to characterize methylation rates in the reservoir and any nearby wetland areas, and the distribution of mercury in the reservoir and tributary sediments.

Sanchez Reservoir Objectives

The overall objective of the Sanchez Reservoir sampling effort is to support the development of a mercury TMDL by quantifying sources of mercury loading to the reservoir and by understanding the mercury cycling within the reservoir. Specific objectives include 1) the characterization of discharges from the Battle Mountain Gold Mine and other nearby abandoned mines that could impact tributaries to Sanchez, 2) the characterization of mercury in water column, macroinvertebrates, and sediments from the tributaries and an irrigation canal leading to Sanchez, 3) the characterization of potential methylation in wetlands along Ventero Creek and the reservoir, and 4) the characterization of the reservoir sediments, macroinvertebrates, and water quality. Fish will be collected in the reservoir. Along with assisting the TMDL project described in this plan, coordination with the US Fish and Wildlife Service (USFWS), the Colorado Dept. of Wildlife (CDOW) and Colorado Dept. of Public Health and Environment (CDPHE) Water Quality Control Division should assist the state's monitoring program and the CDOW fish advisory program.

Previous water quality and sediment sampling was conducted in 1994 for EPA in Sanchez Reservoir and several tributaries and irrigation canals to the reservoir. Limited water quality data were also collected for EPA in 1992. Fish sampling was conducted by CDOW in 1991 and by USFWS in 1992, and showed elevated mercury concentrations in many of the fish samples. The Battle Mountain Gold Mine is located northeast of the reservoir and discharges from this mine may affect the reservoir via Culebra Creek and Sanchez Canal. Other historic mining operations may have occurred in the mountains east of the reservoir. Placer mining for gold was practiced in the northern part of the county in the 1930's, and mercury for amalgamation may have been used. No ultra-clean sampling for mercury of the reservoir or tributaries has been conducted previously. This sampling event in the summer of 1999 should determine if mine discharges are a significant source of mercury loading to the reservoir. The new sampling data will also determine whether irrigation return flow or logging operations are other significant mercury sources within the watershed. This sampling trip should also provide data needed to characterize methylation rates in the reservoir and associated wetlands and the distribution of mercury in the reservoir and tributary sediments.

2.0 SITE LOCATION AND BACKGROUND

McPhee and Narraguinne Reservoirs are located in Montezuma County in southwestern Colorado near the Four Corners area. Part of McPhee is within the boundaries of the San Juan National Forest. McPhee Reservoir was completed in 1986 and is part of the Dolores Irrigation Project of the USBR. Narraguinne Reservoir was built in 1907 and was enlarged in 1956; the reservoir is now part of the Montezuma Valley Irrigation Company. The general location of the three reservoirs is shown in Figure 1. Maps of the reservoirs and watersheds are provided as Figures 2 and 3.

Parts of the Dolores River watershed (inflow to McPhee and Narraguinne Reservoirs) have been mined since the 1870's. Gold, silver, copper, and other precious metals have been obtained from hard-rock mines in and around the watershed. Elevated mercury levels from wastes and surface waters near some abandoned and active mines have been documented. Limited oil/gas exploration and operations and coal mining have also occurred in the general area of these reservoirs. Irrigated agriculture and grazing are a major land use around Narraguinne Reservoir.

Documentation of elevated mercury in fish from McPhee and Narraguinne Reservoirs occurred beginning in 1989, as a result of fish sampling in the reservoirs by CDOW and USFWS. The cause(s) of these mercury problems is currently unknown. The most likely mercury sources include: abandoned mines, atmospheric deposition, natural background from mineralized soils, irrigation return flows, and releases associated with oil/gas exploration and/or operations.

Sanchez Reservoir is located in southern Colorado in Costilla County. The reservoir was built in 1912 by a private irrigation company. Ownership was transferred to the Sanchez Ditch and Reservoir Company in 1956. Management of the fishery at the reservoir by CDOW began in 1978. The reservoir is part of the Sanchez State Wildlife Area. A map of the reservoir and nearby watershed is shown in Figure 4.

Recent gold mining has occurred northeast of Sanchez Reservoir (e.g., the Battle Mountain Gold Mine) and discharges from this area may be affecting the reservoir. Other historic mines for gold and silver may be present in the mountains east of the reservoir. Placer mining for gold was practiced in the northern part of the county in the 1930's, and mercury for amalgamation may have been used. Irrigation return flows also discharge to the reservoir.

Documentation of elevated mercury in fish from Sanchez Reservoir occurred beginning in 1991, as a result of fish sampling in the reservoir by CDOW. The cause(s) of these mercury problems is currently unknown. The most likely mercury sources include: abandoned mines, atmospheric deposition, natural background from mineralized soils, irrigation return flows, and possibly runoff from timber cutting operations. In addition, extensive wetlands border the major inflowing tributary to this reservoir and exist along one side of the reservoir. Thus, in-situ methylation of mercury could be significant.

2.1 Previous Investigations and Regulatory Involvement

McPhee Reservoir

Fish sampling was conducted in 1989 and 1991 by CDOW and by USFWS in 1990 and 1991. A total of twelve fillet samples were collected; mercury tissue concentrations as wet weight ranged from 0.11 mg/kg in a 6-12 in long rainbow trout to 0.73 mg/kg in a 12-18 inch long largemouth bass. The average of the 12 samples was 0.34 mg/kg. Two largemouth bass and one black crappie had tissue concentrations above the state human consumption criteria (0.5 mg/kg). Thirteen wholebody fish samples were also collected. The range of mercury tissue concentrations as wet weight was 0.08 mg/kg in a 12-18 Kokanee salmon to 0.68 mg/kg in a 15 inch long smallmouth bass. The lake was listed as impaired; a fishing advisory was posted in 1991.

In 1994, routine screening under CERCLA was conducted by contractors for EPA (EPA, 1994a). Three water samples were collected from McPhee Reservoir and eight water samples were collected from inflows to the reservoir including the Dolores River, Lost Canyon Creek, Plateau Creek, Dry Creek, Beaver Creek, and House Creek. These samples were analyzed for total mercury; all samples were below the detection limit for total mercury of 0.0002 mg/l. Sediment samples were also collected at the same time as the water samples from the same locations. The sediment samples were all below the detection limit for total mercury; detection limits varied from 0.08 mg/kg to 0.14 mg/kg.

Dissolved mercury was analyzed by the USGS in the outflow from McPhee Reservoir in 1990, but was below the detection limit for dissolved mercury of 0.0002 mg/L (Butler, et al, 1995). Samples of the Dolores River were collected by the USGS at several locations in 1992. Total mercury was detected in the water at concentrations up to 0.00035 mg/L. Sediment samples were collected by the USGS in 1989 and 1993 in the Dolores River. The highest total mercury concentration was 0.55 mg/kg at one of the tributaries receiving mine discharges.

Water quality samples were collected by the USGS from McPhee Reservoir outflow in May and August 1990 (Butler et al, 1995). The water had alkaline pH (8.2 to 8.3), calcium of 40 to 44 mg/L, chloride of 8 to 9 mg/L, and sulfate of 24 to 30 mg/L.

There are over 400 mines/millsites that have been identified in the Dolores River watershed. Mercury was detected in the water column or sediment at 16 locations along the river. More detailed information on these mines will be provided in the final version of the report "Review of Mercury Data and Related Information for Six Colorado Reservoirs" prepared for this project.

Narraguinnep Reservoir

Fish sampling was conducted in 1989 by CDOW. Nine fillet samples were collected; mercury tissue concentrations as wet weight ranged from 0.05 mg/kg in a 24 in long channel catfish to 1.2 mg/kg in a 18-24 inch long walleye. The average of the nine samples was 0.58 mg/kg. Two walleye and three northern pike had tissue concentrations above the state human

consumption criteria (0.5 mg/kg). The range of mercury tissue concentrations as wet weight was 1.2 to 1.6 mg/kg in fillet samples and 0.17 to 0.65 mg/kg in wholebody samples. This reservoir receives inflow from an impaired waterbody (McPhee); a fishing advisory at Narraguinnep was posted in 1991. Limited fish sampling was conducted in 1988 by the USBR showing elevated mercury in three fillet samples.

In 1994, routine screening under CERCLA was conducted by contractors for EPA (EPA, 1994a). Three water and sediment samples were collected from Narraguinnep Reservoir and one water and sediment sample from the outflow from MCPhee Reservoir were collected. These samples were analyzed for total mercury; all samples were below the detection limit for total mercury of 0.0002 mg/l. The sediment samples were also below the detection limit for total mercury; detection limits varied from 0.06 mg/kg to 0.08 mg/kg.

Dissolved mercury was analyzed by the USGS in the outflow from MCPhee Reservoir in 1990, but was below the detection limit for dissolved mercury of 0.0002 mg/L (Butler, et al, 1995). This is the current inflow to Narraguinnep Reservoir. The previous inflow was from the Dolores River, which has had detected total and dissolved mercury, as noted above.

Two water quality samples were collected at the reservoir outlet, one in August 1977 and one in May 1980. These data show alkaline pH (6.8 and 8.1) and calcium of 3.3 and 73 mg/L. Dissolved iron was measured only in 1977 and was 0.4 mg/L. Sediment samples have not been collected from the reservoir.

Sanchez Reservoir

Fish sampling at Sanchez was conducted by CDOW in 1991 and 1993 and by USFWS in 1992. All samples were filets. The mercury fish tissue concentrations ranged from 0.05 mg/kg in a 6 to 12 inch long brown trout to 2.17 mg/kg in a 17 inch long walleye. The average mercury concentrations in the 20 samples was 0.83 mg/kg. Ten of the samples exceeded the state criteria of 0.5 mg/kg. The reservoir was listed as impaired; fish advisories were set in 1994.

In 1994, routine screening under CERCLA was conducted by contractors for EPA (EPA, 1994b). Four water samples from the reservoir were collected for this project and analyzed for total mercury. All the water samples were below the detection limit for total mercury of 0.0002 mg/L. Mercury water samples were also collected by the EPA contractors at 14 locations on tributaries to Sanchez for this routine CERCLA screening project. No total mercury was detected in any of the aqueous samples; the detection limit for total mercury was 0.0002 mg/L. Sediment samples were collected from the same locations as the water samples and at the same time. All the sediment samples also had no detected total mercury. However, detection limits for total mercury varied from 0.11 to 0.26 mg/kg dry weight.

Up to six water quality samples were collected from the reservoir, but only a few parameters of interest to this investigation were measured. The water was alkaline (pH of 8.6 to 9.2, alkalinity of 84 to 88 mg/L) and had total iron of 0.019 to 0.17 mg/L and chlorophyll *a*. of 0.002 to 0.06 mg/L.

Recent gold mining occurred in the mountains northeast of the reservoir and historic gold mining may have occurred east of Sanchez Reservoir. The nearest mine that may affect the reservoir is Battle Mountain Gold Mine. Routine screening under CERCLA was conducted by EPA contractors at this mine in 1995 (EPA, 1995). The highest total mercury concentration of 0.0013 mg/l was measured in mine wastewaters in a sample collected on 9/13/91 from the on-site leachate collection pond. Quarterly sampling data of surface waters and groundwaters on and near the mine are also available from the Colorado Division of Mines and Geology from 1991 to March 1999. Elevated total mercury concentrations have been detected in surface waters and groundwaters at the mine site. For example, total mercury was detected in samples from the Rito Seco River collected in July 1993 at a concentration of 0.0004 mg/l on the mine property and at 0.0005 mg/l at a location on the downstream property boundary (CDMG, 1994). Two groundwater samples collected in the summer of 1994 from two downgradient wells near the mine had total mercury concentrations up to 0.0005 mg/l (CDMG, 1994). The Rito Seco River does not discharge directly into the Sanchez Reservoir, but these data are indicators that mercury has affected nearby surface and ground waters.

3.0 MAPS AND FIGURES

Figure 1: General location of reservoirs investigated

Figure 2: Regional location map of Dolores River Basin

Figure 3: Map of McPhee and Narraguinnep Reservoirs

Figure 4: Map of Sanchez Reservoir and Vicinity
(see Attachment 1)

4.0 SAMPLING PLAN

4.1 MCPHEE RESERVOIR WATERSHED SAMPLING

Mercury sampling within the watershed will include water and sediment sampling of potential mercury sources including mine discharges, an old dump site, a former sulfuric acid production plant, and sewage treatment ponds; small tributaries where mercury has been detected in past sampling, and the two rivers providing flow to McPhee Reservoir. All of these water and sediment samples will be analyzed for total mercury and particulate mercury in order to characterize the major mercury sources within the watershed. Total organic carbon (TOC) content and grain size will also be measured to help define the mercury's mobility and distribution within the watershed. Sulfides will be analyzed in the sediment to determine extent of mine input and redox conditions. It is estimated that 17 total mercury, TOC, sulfide, and grain size sediment samples will be collected for source characterization purposes. An estimated 17 water samples will be collected and analyzed for total mercury, major cations/anions, alkalinity, total dissolved solids, and total suspended solids. Field measurements in the water samples will include pH, conductivity, temperature, turbidity, redox potential, and dissolved oxygen. This number (17) was arrived at by reviewing the past sampling data and information on mines and other sources. The sampling locations include three mine drains, an old dump site, a former sulfuric acid production plant, sewage treatment effluent ponds, five tributaries where mercury has been detected in the past (Horse Creek, Deadwood Creek, Rio Lado, Garrison Canyon, and Lost Canyon), Bear Creek where past mining occurred, three samples on the main-stem of the Dolores River, and two on the West Dolores River. These locations are shown in Figure 5 (Attachment 1).

4.2 MCPHEE RESERVOIR SAMPLING

Water and sediment samples will be collected at four locations shown in Figure 6 to help characterize the mercury cycling and the mercury distribution in McPhee Reservoir. Water sampling will precede sediment sampling because sediment sampling may re-suspend sediments into the water column. A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates from the Dolores River above the treatment ponds and at the inlet to the reservoir, the shallow area near the House Creek inlet, and the shallow reservoir area near the inlet on the northern side of the reservoir.

4.2.1 Water

General Water Quality

At the four reservoir sampling locations, shown in Figure 6, and in front of the dam, dissolved oxygen (DO), temperature, pH, turbidity, redox potential, and conductivity profiles will be measured and recorded to determine if the reservoir is stratified into distinct layers (epilimnion, hypolimnion). Instruments will be calibrated prior to use each day. Samples for general water

quality parameters will be collected from approx. 1 foot above and below the epilimnion and hypolimnion interface. General water quality parameters will include: cations, anions, alkalinity, total suspended solids (TSS), total dissolved solids (TDS), dissolved organic carbon (DOC), and chlorophyll *a*.

Mercury

Unfiltered water samples for total mercury and particulate mercury will be collected at the four locations in the reservoir from approx. 1 foot above and below the epilimnion/hypolimnion interface. Since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2×10^{-9} mg/L or less. Water samples will also be collected and filtered in the field using ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved mercury.

Methyl Mercury

Unfiltered MeHg and samples will be collected at the same four locations just below (approx. 1 foot) the oxic-anoxic boundary in the water column and 1 foot below the water surface. Again, since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2×10^{-9} mg/L or less. Extra water samples will also be collected at each of the reservoir sampling locations and filtered using pre-cleaned ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved MeHg.

4.2.2 Sediment

After the water samples are collected, sediment grab or core samples will be taken from four different locations, depending on the depth and bottom type. Each grab sample will be of the top 2 cm of sediment. If floc is present above the sediment, a pump will be used to collect this material. All sediment samples will be analyzed for total mercury, methyl mercury, TOC, grain size, sulfide, sulfate, and pH. The pH will be measured in the field immediately after sediment collection.

4.2.3 Macroinvertebrates

A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates from the Dolores River above the treatment ponds and at the inlet to the reservoir, the shallow area near the House Creek inlet, and the shallow reservoir area near the inlet on the northern side of the reservoir. The sediment samples will be collected using an Eckman Grab and then screened to obtain the macroinvertebrates. In the stream settings, a drift net will also be used to capture any disturbed animals or floating insects. The four macroinvertebrate samples will be analyzed for total mercury. Total biomass weight and moisture content will also be determined.

4.3 NARRAGUINNEP RESERVOIR WATERSHED SAMPLING

Mercury sampling within the watershed will include water and sediment sampling of potential mercury sources including the inflow from McPhee Reservoir, two small tributaries, and a nearby irrigation canal. These water and sediment samples will be analyzed for total and particulate mercury in order to characterize the loading from these potential mercury sources. Total organic carbon (TOC) content and grain size will be measured in the sediment samples to help define the mercury's mobility and distribution within the watershed. Sulfides will be analyzed in the sediment to determine extent of mine input and redox conditions. It is estimated that four total mercury, TOC, sulfide, and grain size sediment samples will be collected for source characterization purposes. An estimated four water samples will be collected and analyzed for total mercury, major cations/anions, alkalinity, total dissolved solids, and total suspended solids. Field measurements in the water samples will include pH, conductivity, temperature, turbidity, redox potential, and dissolved oxygen. This number (4) was arrived at by reviewing the watershed map and information on other sources. The sampling locations include the inflow from McPhee Reservoir, two small tributaries draining agricultural areas, and a nearby irrigation canal. These locations are shown in Figure 7 (Attachment 1).

4.4 NARRAGUINNEP RESERVOIR SAMPLING

Water and sediment samples will be collected at four locations in the reservoir, also shown in Figure 7, to help characterize the mercury cycling and the mercury distribution in Narraguinnep Reservoir. Water sampling will precede sediment sampling because sediment sampling may re-suspend sediments into the water column. A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates at the inflow from McPhee Reservoir, the larger of the two inlets in the agricultural area, and the shallow reservoir area near the inlet from McPhee.

4.4.1 Water

General Water Quality

At the four locations in the reservoir, shown in Figure 7, and in front of the dam, dissolved oxygen (DO), temperature, pH, turbidity, redox potential, and conductivity profiles will be measured to determine if the reservoir is stratified into distinct layers (epilimnion, hypolimnion). Samples for general water quality parameters will be collected from approx. 1 foot above and below the epilimnion and hypolimnion interface. General water quality parameters will include: cations, anions, alkalinity, total suspended solids (TSS), total dissolved solids (TDS), dissolved organic carbon (DOC), and chlorophyll *a*.

Mercury

Unfiltered water samples for total mercury and particulate mercury will be collected at the four locations from approx. 1 foot above and below the epilimnion/hypolimnion interface. Since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2×10^{-9} mg/L or less. Water samples will also be collected at each reservoir sampling location and filtered in the field using ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved mercury.

Methyl Mercury

Unfiltered MeHg samples will be collected at the same four locations just below (approx. 1 foot) the oxic-anoxic boundary in the water column and 1 foot below the water surface. Again, since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2×10^{-9} mg/L or less. Extra water samples will also be collected at each of the reservoir sampling locations and filtered using pre-cleaned ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved MeHg and particulate Hg.

4.4.2 Sediment

After the water samples are collected, sediment grab or core samples will be taken from three different locations, depending on the depth and bottom type. Each grab sample will be of the top 2 cm of reservoir sediment. If floc is present above the sediment, a pump will be used to collect this material. All sediment samples will be analyzed for total mercury, methyl mercury, TOC, grain size, sulfate, sulfide, and pH. The pH will be measured in the field immediately after sediment collection.

4.4.3 Macroinvertebrates

A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates at the inflow from McPhee Reservoir, the larger of the two inlets in the agricultural area, and the shallow reservoir area near the inlet from McPhee. The sediment samples will be collected using an Eckman Grab and then screened to obtain the macroinvertebrates. In the stream settings, a drift net will also be used to capture any disturbed animals or floating insects. The four macroinvertebrate samples will be analyzed for total mercury. Total biomass weight and moisture content will also be determined.

4.5 SANCHEZ RESERVOIR WATERSHED SAMPLING

Mercury sampling within the watershed will include water, macroinvertebrates, and sediment sampling of potential mercury sources including two locations on Ventero Creek, eight tributaries - Culebra, Vallejos, San Francisco, Toricido, Jaroso, Cutes, and Willow creeks, a seep to Sanchez Canal north of San Francisco Creek, a mine drainage canal from the Battle Mountain Gold Mine, and Sanchez Canal. Three wetland samples will also be collected. The locations of these sampling points are shown in Figure 8. These water, macroinvertebrates, and sediment samples will be analyzed for total mercury in order to characterize the loading from these potential mercury sources. Total organic carbon (TOC) content and grain size will be measured in the sediment samples to help define the mercury's mobility and distribution within the watershed. Sulfides will also be analyzed in the sediment to determine extent of mine input and redox conditions. It is estimated that thirteen total mercury, TOC, sulfide, and grain size sediment samples will be collected for source characterization purposes. An estimated thirteen water samples will be collected and analyzed for total mercury, particulate mercury, major cations/anions, alkalinity, total dissolved solids, and total suspended solids. Field measurements in the water samples will include pH, conductivity, temperature, turbidity, redox potential, and dissolved oxygen. Surface water and porewater from three locations in the wetlands along Ventero Creek will be collected and analyzed for TOC, DOC, and the above water parameters. The total number of samples (16) was arrived at by reviewing the watershed map and information on mining and other sources. The sampling locations include the inflow from Ventero Creek, all the tributaries to the reservoir and a nearby irrigation canal and mine discharge canal. These locations are shown in Figure 8 (Attachment 1).

4.6 SANCHEZ RESERVOIR SAMPLING

Water and sediment samples will be collected at three locations in the reservoir, also shown in Figure 8, to help characterize the mercury cycling and the mercury distribution in Sanchez Reservoir. Water sampling will precede sediment sampling because sediment sampling may re-suspend sediments into the water column. A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates at the inflow from Ventero Creek, the eight tributaries, and the shallow reservoir area near the inlet from Sanchez Canal.

4.6.1 Water

General Water Quality

At the three locations in the reservoir, shown in Figure 8, and in front of the dam, dissolved oxygen (DO), temperature, pH, turbidity, redox potential, and conductivity profiles will be measured to determine if the reservoir is stratified into distinct layers (epilimnion, hypolimnion). Samples for general water quality parameters will be collected from approx. 1 foot above and below the epilimnion and hypolimnion interface. General water quality parameters will include: cations, anions, alkalinity, total suspended solids (TSS), total dissolved solids (TDS), dissolved organic carbon (DOC), and chlorophyll *a*.

Mercury

Unfiltered water samples for total mercury will be collected at the same four locations in the reservoir from approx. 1 foot above and below the epilimnion/hypolimnion interface. Since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2×10^{-9} mg/L or less. Water samples will also be collected and filtered in the field using ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved mercury.

Methyl Mercury

Unfiltered MeHg samples will be collected at the same four locations just below (approx. 1 foot) the oxic-anoxic boundary in the water column and 1 foot below the water surface. Again, since mercury in the water column is expected to be in very low concentrations, the collection of these water samples will require ultra-clean sampling techniques, and the analytical method for these water samples will have a detection limit of 0.2 ng/L or less. Extra water samples will also be collected and filtered using pre-cleaned ($<0.45 \mu\text{m}$ pre-cleaned filters) for analysis of dissolved MeHg.

4.6.2 Sediment

After the water samples are collected, sediment grab or core samples will be taken from three different locations, depending on the depth and bottom type. Each grab sample will be of the top 2 cm of sediment. If floc is present above the sediment, a pump will be used to collect this material. All sediment samples will be analyzed for total mercury, methyl mercury, TOC, grain size, sulfide, sulfate, and pH. The pH will be measured in the field immediately after sediment collection.

4.6.3 Macroinvertebrates

A separate sediment sample of the top 5 cm will be collected to obtain macroinvertebrates at the inflow from Ventero Creek, the eight tributaries listed above, and the shallow reservoir area near the inlet from Sanchez Canal. The sediment samples will be collected using an Eckman Grab and then screened to obtain the macroinvertebrates. In the stream settings, a drift net will also be used to capture any disturbed animals or floating insects. The ten macroinvertebrate samples will be analyzed for total mercury. Total biomass weight and moisture content will also be determined.

5.0 REQUEST FOR ANALYSES

Methods selected below will provide the required precision, accuracy, and detection limits to meet the objectives of this project. Also field measurements will be performed by qualified individuals with calibrated instruments and within appropriate hold times.

Table 1. Summary of sampling, analytical labs, and analytical methods

parameter	# of samples	analytical laboratory	analytical method
McPhee Reservoir Watershed			
<u>water</u>			See footnote a
major constituents**	17	Class 100 Lab	EPA 1631, 0.2 ng/L (pp trillion)
total Hg (unfilt.)	17	Class 100 Lab	EPA 1631, 0.2 ng/L (pp trillion)
particulate Hg	17	Class 100 Lab	EPA 1631, 0.2 ng/L (pp trillion)
dissolved Hg (filt.)	17	Class 100 Lab	EPA 1631, 0.2 ng/L (pp trillion)
<u>sediments</u>			
total Hg	17	Class 100 Lab	EPA 1631, DL=0.5 ng/g (ppb)
TOC	17	Class 100 Lab	EPA 9060 modified for solids
grain size	17	Class 100 Lab	ASTM D422-63
sulfide	17	Class 100 Lab	SWMM 4500-S ²

McPhee Reservoir			
<u>water</u> profile*	multiple depths	field measurements	-
major constituents**	8	Class 100 Lab	see footnote b
TSS	8	Tetra Tech	EPA Method 160.2
chlorophyll a	8	Tetra Tech	SM 10200 H
total Hg (unfilt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
particulate Hg	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved Hg (filt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
total MeHg (unfilt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved MeHg (filt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
<u>sediments</u>		Class 100 Lab	EPA 1631, DL = 0.5 ng/g (ppb)
total Hg	4	Class 100 Lab	EPA 1631, DL = 0.02 ng/g (ppb)
MeHg	4	Class 100 Lab	EPA Method 300.0
sulfate	4	Class 100 Lab	SWMM 4500-S ²
sulfide	4	Class 100 Lab	EPA 9060 modified for solids
TOC	4	field measurements	ASTM D422-63
grain size	4	field measurements	-
pH (field meas.)	4		
<u>macroinvertebrates</u>		Class 100 Lab	EPA 1631, DL = 0.5 ng/g (dry wt)
total Hg	4		
Narraguinnep Reservoir Watershed			
<u>water</u> profile*	multiple depths	field measurements	-
major constituents**	4	Class 100 Lab	see footnote a
total Hg (unfilt.)	4	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
particulate Hg	4	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved Hg (filt.)	4	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
<u>sediments</u>		Class 100 Lab	EPA 1631, DL = 0.5 ng/g (ppb)
total Hg	4	Class 100 Lab	EPA Method 300.0
sulfide	4	Class 100 Lab	EPA 9060 modified for solids
TOC	4	Class 100 Lab	ASTM D422-63
grain size	4	Class 100 Lab	-
pH (field meas.)	4	field measurements	

Narraguinnep Reservoir			
<u>water</u> profile*	multiple depths	field measurements	-
major constituents**	8	Class 100 Lab	see footnote b
TSS	8	Tetra Tech	EPA Method 160.2
chlorophyll a	8	Tetra Tech	SM 10200 H
total Hg (unfilt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
particulate Hg	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved Hg (filt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
total MeHg (unfilt.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved MeHg (unfil.)	8	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
<u>sediments</u>			
total Hg	4	Class 100 Lab	EPA 1631, DL = 0.5 ng/g (ppb)
MeHg	4	Class 100 Lab	EPA 1631, DL = 0.2 ng/g (ppb)
sulfate	4	Class 100 Lab	EPA Method 300.0
sulfide	4	Class 100 Lab	SMWW 4500-S ²⁻
TOC	4	Class 100 Lab	EPA 9060 modified for solids
grain size	4	Class 100 Lab	ASTM D422-63
pH (field meas.)	4	field measurements	-
<u>Macroinvertebrates</u>			
Total Hg	4	Class 100 Lab	EPA 1631, DL = 0.5 ng/g (dry wt)

Sanchez Reservoir			
<u>water</u> profile*	multiple depths	field measurements	-
major constituents**	6	Class 100 Lab	see footnote b
TSS	6	Tetra Tech	EPA Method 160.2
chlorophyll a	6	Tetra Tech	SM 10200 H
total Hg (unfilt.)	6	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
particulate Hg	6	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved Hg (filt.)	6	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
total MeHg (unfilt.)	6	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
dissolved MeHg (unfil.)	6	Class 100 Lab	EPA 1631, DL = 0.2 ng/L (pp trillion)
<u>sediments</u>			
total Hg	3	Class 100 Lab	EPA 1631, DL = 0.5 ng/g (ppb)
MeHg	3	Class 100 Lab	EPA 1631, DL = 0.2 ng/g (ppb)
sulfate	3	Class 100 Lab	EPA Method 300.0
sulfide	3	Class 100 Lab	SMWW 4500-S ²⁻
TOC	3	Class 100 Lab	EPA 9060 modified for solids
grain size	3	Class 100 Lab	ASTM D422-63
pH (field meas.)	3	field measurements	-
<u>Macroinvertebrates</u>			
Total Hg	10	Class 100 Lab	EPA 1631, DL = 0.5 ng/g (dry wt)

*profile: DO, temperature, pH, turbidity, redox potential, conductivity

**major constituents:

cations: CLP SOW ILM03.0 Ca, Mg, Na, K, NH₄
anions: EPA Method 300.0 Cl, NO₂, NO₃, T-PO₄, SO₄
alkalinity: Standard Methods 2320
total dissolved solids (TDS): EPA Method 160.1

^aTributary water samples analyzed for above parameters

^bReservoir water samples for above parameters and DOC and chlorophyll a
dissolved organic carbon (DOC): EPA Method 415.1; chlorophyll a SM 10200 H

^cWetland surface water and porewater samples analyzed for major constituents, TOC (EPA Method 9060) and DOC

6.0 METHODS AND PROCEDURES

This section describes the methods and procedures that will be used to collect samples including samples needed to prepare QA/QC samples. All samples will be handled in accordance with EPA procedures and chain-of-custody guidelines. Trace metal “ultra-clean” procedures will be used to collect samples for mercury analyses. These special precautionary measures are described in EPA method 1669; they are designed to eliminate potential sample contamination from sample equipment or sampler disregard for cross-contamination. Containers will be pre-cleaned prior to sample collection. Polyethylene equipment will be used to collect soil and sediment samples. All Hg samples in containers will be labeled, sealed with tape, and placed in coolers for transport to the contracted lab. QA/QC procedures are discussed in Section 8.0.

All other samples can be collected without regard for trace metal contamination. These samples will be collected in polyethylene or glass bottles and preserved as specified in Section 7.2. The containers will be labeled, sealed with tape, and placed in coolers for transport to a Class 100 Laboratory or the appropriate EPA-approved contract laboratory.

6.1 Tributary Sampling

6.1.1 Water Sampling

Trace metal clean techniques (as described in EPA Method 1669) will be used throughout collection of water samples. Tributary water samples will be collected as grab samples into 1-liter plastic bottles for standard parameters while submerged under the water surface, and into acid cleaned 1-liter Teflon bottles for mercury. Samplers will don disposable polyethylene gloves prior to collection of all mercury samples. Each bottle will be rinsed with the sample water (3x) prior to collection. Pre-cleaned filters will be used to produce filtered ($<0.45\ \mu\text{m}$) samples. Filtration equipment may involve additional containers (sometimes referred to as intermediate vessels); these will be rinsed 3x with sample water prior to filtrate collection. Each bottle will be filled completely and placed inside two plastic bags. After sample containers are filled, they will be immediately sealed and placed in an insulated cooler with ice and shipped to the appropriate lab (Table 1). Water samples for mercury analyses will be transported to the Class 100 laboratory and samples for major constituent analyses will be sent to the Class 100 Laboratory.

Total, particulate and dissolved mercury water samples will be collected and sent to the laboratory in separate 1-liter acid-cleaned Teflon bottles. Other water quality parameters will be collected and sent to the laboratory in 500 mL HDPE bottles. (See Table 2 in Section 7.)

6.1.2 Sediment Sampling

Watershed tributary sediment samples will be collected with short non-metallic gravity corers or polyethylene scoops and stored in (quality assurance tested) glass jars with air tight fitting (Teflon lined) lids. Individual Hg sample sizes will consist of at least 1 gram, yet more quantity will be collected if possible. Hg collection will be in 4 oz amber jars (1/4 -1/2 inch of sample).

Individual TOC, sulfide, and grain size samples will consist of 250 g of sample. Grain size and TOC collection will be in 16 oz glass jars (approx. half full of sample). The sulfide sample will be placed in a 250 g glass jar.

6.2 Reservoir Water Sampling

Trace metal clean techniques (as described in EPA Method 1669) will be used throughout collection of lake water samples. Water samples will be collected as grab samples with the aid of a pump attached to acid cleaned Teflon tubing. Each bottle will be rinsed with the sample water (3x) prior to collection. Pre-cleaned filters will be used to produce filtered (0.45 um) samples. Filtration equipment may involve additional containers (sometimes referred to as intermediate vessels); these will be rinsed 3x with sample water prior to filtrate collection. Each bottle will be filled completely and placed inside two plastic bags. After sample containers are filled, they will be immediately sealed and placed in an insulated cooler with ice. As soon as all samples are collected they will be transported to the Class 100 Laboratory. Water samples for mercury analyses will be transported to the Class 100 Laboratory.

Total, particulate and dissolved mercury water samples will be collected and sent to the laboratory in separate 1-liter acid-cleaned Teflon bottles. Other water quality parameters will be collected and sent to the laboratory in 500 mL HDPE bottles. (See Table 2 in Section 7.)

6.3 Reservoir Sediment Sampling

Reservoir sediments in shallow water (less than 2 feet deep) will be sampled with a short non-metallic gravity corer and will consist of the top 2 cm of lake bed sediment. Reservoir sediments in deeper waters (more than 2 feet deep) will be sampled with a core or petite Ponar grab and will also consist of the top 2 cm of reservoir sediment. If a floc is present at the sediment-water interface, a sample will be pumped using acid-cleaned Teflon tubing into a 1-liter Teflon bottle to obtain a sample for total and methyl mercury analysis only.

Individual Hg sample sizes will consist of at least 1 gram, yet more quantity will be collected if possible. Hg sediment samples will be placed in 4 oz amber jars (1/4 -1/2 inch of sample).

Individual TOC, sulfide, and grain size samples will consist of 250 g. Grain size and TOC collection will be in 16 oz glass jars (approx. half full of sample). Individual sulfate sample sizes will consist of at least 100 grams. Sulfate collection will be in 4 oz jars.

6.4 Macroinvertebrates

Insects and other mobile animals like amphipods that have emerged from the sediments or rocks will be collected using a drift net. Stationary animals and larval insects in the sediments will be collected by first obtaining a sediment sample using an Eckman grab sampler and then screening the sediment with a Nytex 300 um mesh size to obtain the animals. The types of animals obtained will be recorded in the bound field logbook. The animals will be placed in acid-

cleaned 20-ml Teflon bottles. The samples will be transported to the laboratory for total mercury analysis. Biomass weight and moisture content will also be determined. A description of these procedures is included in Attachment 2.

6.5 Field Equipment Blanks

Field equipment blanks will be collected for sediment, macroinvertebrates, and water samples. For macroinvertebrate and sediment samples, these blanks will consist of rinsates of the sampling equipment (e.g., corer) with high purity water. Water equipment blanks shall be collected using the pump and tubing and ultra-clean water supplied by the Class 100 laboratory.

6.6 Temperature Blanks

In order to evaluate potential effects of sample transportation and handling on data quality, a thermal temperature sensor will be used to record the temperature of the samples when received.

6.7 Collection of Duplicate Samples

Extra water and sediment samples will be collected to prepare blind duplicate water and sediment samples at a rate of one sample of each type per twenty samples. A double volume of water and sediment will be collected for use by the laboratory in preparing MS/MSD samples at a rate of one MS/MSD set per twenty samples.

6.8 Decontamination Procedures

Pesticide grade solvent rinse (highest purity methanol) will be used to rinse polyethylene scoops, spatulas, petite Ponar grabs, and corers prior to collecting sediment samples. Sediment corer or the petite Ponar grab equipment will also be rinsed with reservoir or tributary water which will contain mercury at levels several orders of magnitude below the sediments. Dedicated equipment will be used for collecting water samples, which are believed to yield the lowest mercury concentrations. The collection order of water samples at a single location will be to take surface samples first then those that are deep so as to avoid cross contamination. In addition, sample tubing will be rinsed by pumping water for at least two minutes at the highest flow rate prior to collection of the next samples.

6.9 Fish QA/QC Samples

USFWS and CDOW will collect fish from each reservoir, as described in the fish sampling SOP included in the appendix. The fish will be prepared by their staff as fillets in the field. At least ten percent of the fish fillet samples will be prepared as split samples. These split samples will be analyzed by Frontier Geosciences; the other samples will be analyzed by the CDOW laboratory. The detection limit for the fish tissue analyses is 0.001 mg/kg. All the fillets will be wrapped in aluminum foil and placed in zip-lock bags and placed in a cooler with ice for shipment to the laboratory. The fish samples will be collected at a different time than the water/sediment samples.

7.0 SAMPLE DOCUMENTATION AND SHIPMENT

7.1 Field Documentation

At a minimum, the following information will be recorded during the collection of each sample:

- Sample
- Sampler's name(s)
- Date and time of sample collection
- Field observations and details important to analysis or integrity of samples (e.g., heavy rains, odors, colors, etc.)
- Preliminary sample descriptions (e.g., sediment type, color, odors)
- pH, DO, temperature, conductivity, turbidity, redox potential (for water samples)
- pH (for sediment samples)
- identifiable biota types and condition (macroinvertebrates)
- flow measurements

7.2 Bottles and Preservatives

Sediment and water samples will be chilled to 4°C. Water samples for mercury analyses will be collected in acid-cleaned 1-Liter Teflon bottles and preserved by the Frontier Geoscience lab with 0.5% (trace metal clean) HCl. Water samples for the other analyses will be preserved in the field. Macroinvertebrates will be narcotized using a small amount of club soda and chilled to 4°C.

The number of sample containers, volumes, and materials are listed in Table 2.

Table 2. Sampling containers

description	number and type of sample bottles
RESERVOIR OR TRIBUTARY SEDIMENTS	
total Hg-wet sediment	45 x 4 oz. I-Chem glass jars (wide mouth with teflon lined lid)
MeHg-wet sediment (reservoirs only)	11 (see above total Hg-wet sediment)
sulfide-wet sediment	45 glass jars
sulfate-wet sediment (reservoirs only)	11 glass jars
TOC-wet sediment	45 glass jars
pH-wet sediment (field measurement)	field
RESERVOIR PROFILES	field
temperature-water (field)	
DO profile-water (field)	
pH profile-water (field)	
redox potential (field)	
turbidity-water (field)	
conductivity-water (field)	
WATER CONSTITUENTS	
temperature, pH, DO, turbidity, redox potential-(field)	field
cations	62 x 500 mL HDPE
anions, alkalinity	62 x 1 L HDPE
TSS	22 x 1 L HDPE
TDS	62 x 500 mL HDPE
dissolved organic carbon	28 x 500 mL HDPE
total organic carbon	6 x 500 mL HDPE
chlorophyll a	22 500 mL amber HDPE
total Hg (unfiltered)-water	62 Teflon (FEP) Bottle (500 mL) or I-Chem glass jars
particulate Hg-water	62 Teflon (FEP) Bottle (500 mL) or I-Chem glass jars
total MeHg (unfiltered)-water	22 Teflon (FEP) Bottle (500 mL) or I-Chem glass jars
dissolved Hg (filtered)-water	62 Teflon (FEP) Bottle (500 mL) or I-Chem glass jars
dissolved MeHg (filtered)-water	22 Teflon (FEP) Bottle (500 mL) or I-Chem glass jars
BIOTA	
total Hg/MeHg- macroinvertebrates	17 composites stored in 20 mL glass jars
Total Hg - fish	Split samples of at least 10 percent of fish to be collected by USFWS and CDOW in zip-lock bags

7.3 Sample Traffic Report And Chain-Of-Custody Records, And QA/QC Summary Forms

Chain-of-custody records are used to document sample collection and transportation to the laboratory for analysis. All samples for Class 100, and private lab analyses will be accompanied by a chain-of-custody record. A form will be completed and transported with the samples to each laboratory.

The traffic report and chain-of-custody record will identify the contents of each sample cooler and maintain the custodial integrity of the samples. Generally, a sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, locked up, or kept in a secured area that is restricted to authorized personnel. Until the samples are transported to the individual laboratory, the custody of the samples will be the responsibility of the EPA sampling team. The site leader or designee will sign the chain-of-custody record.

The pink copy of the chain-of-custody record will be sent to the EPA Region 8 Quality Assurance Management Section (QAMS) and the white copy will accompany the samples to the appropriate laboratory. A copy of all of the original chain-of-custody records will be made for the EPA master files.

A quality assurance/quality control (QA/QC) summary form will be completed for each laboratory and each matrix of the sampling event. The sample numbers for all rinsate samples, reference samples, laboratory QC samples, and duplicates will be documented on this form (see Section 8.0). The original form will be sent to QAMS; a photocopy will be made for the EPA master files. This form is not sent to the laboratory.

A self-adhesive custody seal will be placed across the lid of each sample. Samples will be stored in an ice chest to maintain 4°C. These containers will be sealed with self-adhesive custody seals any time they are not in someone's possession or view before transportation. All custody seals will be signed and dated.

Corrections on sample paperwork will be made by placing a single line through the mistake and initialing and dating the change. The correct information will be entered above, below, or after the mistake.

7.4 Labeling, Packaging, And Shipment

All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. The samples will have preassigned, identifiable, and unique numbers. At a minimum, the sample labels will contain the following information: Case Number, station location, date of collection, analytical parameter(s), and method of preservation. Every sample, including samples collected from a single location but going to separate laboratories, will be assigned a unique sample number.

All sample containers will be placed in a strong-outside shipping container. The following outlines the packaging procedures that will be followed for low concentration samples.

1. When ice is used, secure the drain plug of the cooler with fiberglass tape to prevent melting ice from leaking out of the cooler.
2. Line the bottom of the cooler with bubble wrap to prevent breakage during shipment.
3. Check screw caps for tightness and, if not full, mark the sample volume level of liquid samples on the outside of their sample bottles with indelible ink.
4. Secure bottle/container tops with clear tape and custody seal all container tops.
5. Affix sample labels onto the containers with clear tape.
6. Wrap all glass sample containers in bubble wrap to prevent breakage.
7. Seal all sample containers in heavy duty plastic bags. Write the sample numbers on the outside of the plastic bags with indelible ink.

All samples will be placed in coolers with the appropriate chain-of-custody form. All forms will be enclosed in a large plastic bag and affixed to the underside of the cooler lid. Empty space in the cooler will be filled with bubble wrap or styrofoam peanuts to prevent movement and breakage during shipment. Ice used to cool samples will be double sealed in two zip lock plastic bags and placed on top and around the samples to chill them to the correct temperature. Each ice chest will be securely shut, and custody seals will be affixed to the cooler.

Class 100 Lab and EPA 8 Regional Sample Control Centers (RSCC) will be notified daily of the sample shipment schedule (Friday shipments must be reported no later than noon) and will be provided with the following information:

- Sampling contractor's name
- The name and location of the site
- Case number or RAP number
- Total number(s) by concentration and matrix of samples shipped to each laboratory
- Irregularities or anticipated problems associated with the samples
- Whether additional samples will be shipped or if this is the last shipment.

8.0 QUALITY CONTROL

8.1 Duplicate Samples

A duplicate sample will be collected for each group of samples. This will follow EPA field sampling guidelines: one duplicate per twenty samples.

8.2 Laboratory Quality Control Samples

For this sampling event a single sample for the set from Narraguinnep is anticipated, so a double volume of one sample will be collected for the laboratory to prepare MS/MSD samples; that is, duplicate samples will be collected for mercury analyses and duplicates will be collected for other chemical analyses. Double volumes of two samples will be collected for both the McPhee and Sanchez sets for the laboratory to prepare MS/MSD samples.

8.3 Data Validation

The contracted laboratory (for total suspended solids and chlorophyll *a*) will report laboratory blank and matrix spike results for QA/QC. The use of the data does not warrant further validation following the CLP functional guidelines for data review. However, each laboratory will maintain a full data package for data validation should it become appropriate in the future.

8.4 Field Variances

As conditions in the field may vary, it may become necessary to implement minor modifications to sampling as presented in this plan. All variances will be recorded in a bound field notebook.

9.0 Performance Schedule

The water, sediment, and macroinvertebrates will be collected at the same time. Sampling will begin at Sanchez Reservoir on June 3. After sampling this reservoir and the nearby creeks selected for sampling, shown in Figure 8, the sampling team will drive to the McPhee area. Sampling at McPhee Reservoir is expected to begin on June 5th. Narraguinnep Reservoir is planned to be sampled on June 5th or 6th. The Dolores River and other selected upstream tributaries, shown in Figure 5, will be sampled next when both reservoirs are completed. The sampling is expected to be completed by June 8th, but may take 1 or 2 days longer. Standard turn-around time of 3 weeks will be requested from the laboratories. A data report will be prepared one month from receipt of the data from all the laboratories. A phone report will be given to the EPA WAM after the sampling has been completed and to notify EPA that all samples have been received by the laboratories.

10.0 References

Butler, D.L., R.P. Krueger, B.C. Osmendson, and E.G. Jensen. 1995. Reconnaissance Investigation of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Dolores Project Area, Southwestern Colorado and Southeastern Utah, 1990-1991. US Geological Survey Water Resources Investigation Report 94-4041, 126 p.

Colorado Division of Wildlife (CDOW). 1994. File Review of Battle Mountain Gold Mine/San Luis Project Quarterly Sampling Data 1991-1994

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US Environmental Protection Agency (USEPA), 1994a. Site Inspection Analytical Results Report for McPhee and Narraguinnep Reservoirs Dolores, Colorado. Prepared by Morrison Knudsen Corporation, Englewood, Colorado, 33 p.

US Environmental Protection Agency (USEPA), 1994b. Site Inspection Analytical Results Report for Sanchez Reservoir San Luis, Colorado. Prepared by Morrison Knudsen Corporation, Englewood, Colorado, 18 p.

US Environmental Protection Agency (USEPA), 1995. Site Inspection Analytical Results Report for Battle Mountain Gold Mine/San Luis Project San Luis, Colorado. Prepared by Morrison Knudsen Corporation, Englewood, Colorado.

ATTACHMENT 1

Maps and Figures

ATTACHMENT 2

SOP for Ultra-clean Mercury Sampling
SOP for Macroinvertebrate Sampling
SOP for Fish Sampling

All sample containers will be placed in a strong-outside shipping container. The following outlines the packaging procedures that will be followed for low concentration samples.

1. When ice is used, secure the drain plug of the cooler with fiberglass tape to prevent melting ice from leaking out of the cooler.
2. Line the bottom of the cooler with bubble wrap to prevent breakage during shipment.
3. Check screw caps for tightness and, if not full, mark the sample volume level of liquid samples on the outside of their sample bottles with indelible ink.
4. Secure bottle/container tops with clear tape and custody seal all container tops.
5. Affix sample labels onto the containers with clear tape.
6. Wrap all glass sample containers in bubble wrap to prevent breakage.
7. Seal all sample containers in heavy duty plastic bags. Write the sample numbers on the outside of the plastic bags with indelible ink.

All samples will be placed in coolers with the appropriate chain-of-custody form. All forms will be enclosed in a large plastic bag and affixed to the underside of the cooler lid. Empty space in the cooler will be filled with bubble wrap or styrofoam peanuts to prevent movement and breakage during shipment. Ice used to cool samples will be double sealed in two zip lock plastic bags and placed on top and around the samples to chill them to the correct temperature. Each ice chest will be securely shut, and custody seals will be affixed to the cooler.

Class 100 Lab and EPA 8 Regional Sample Control Centers (RSCC) will be notified daily of the sample shipment schedule (Friday shipments must be reported no later than noon) and will be provided with the following information:

- Sampling contractor's name
- The name and location of the site
- Case number or RAP number
- Total number(s) by concentration and matrix of samples shipped to each laboratory
- Irregularities or anticipated problems associated with the samples
- Whether additional samples will be shipped or if this is the last shipment.

ATTACHMENT 1

Maps and Figures

Poor Quality Source Document

The following document images have been scanned from the best available source copy.

To view the actual hard copy, contact the Superfund Records Center at (303) 312-6473.

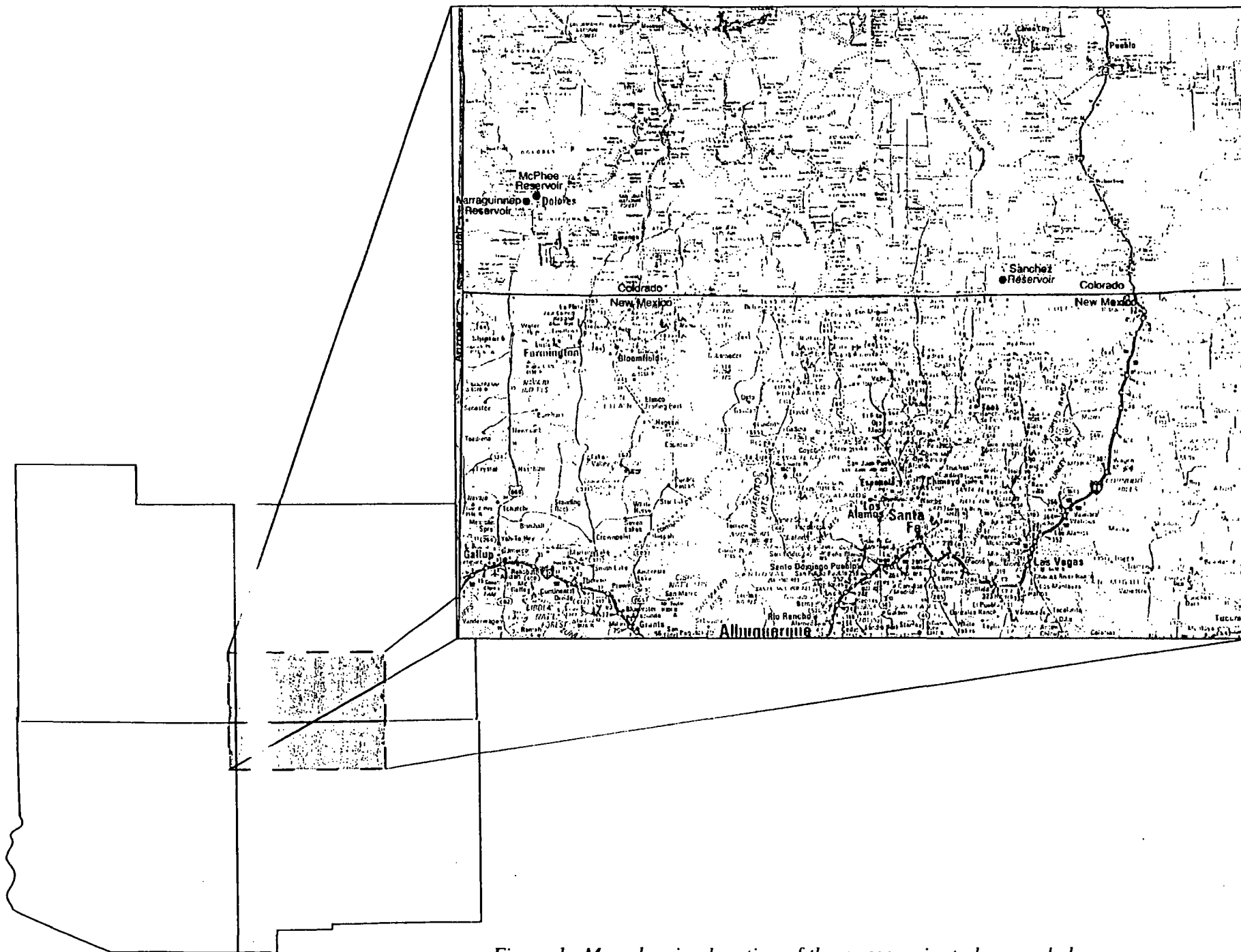


Figure 1. Map showing location of three reservoirs to be sampled

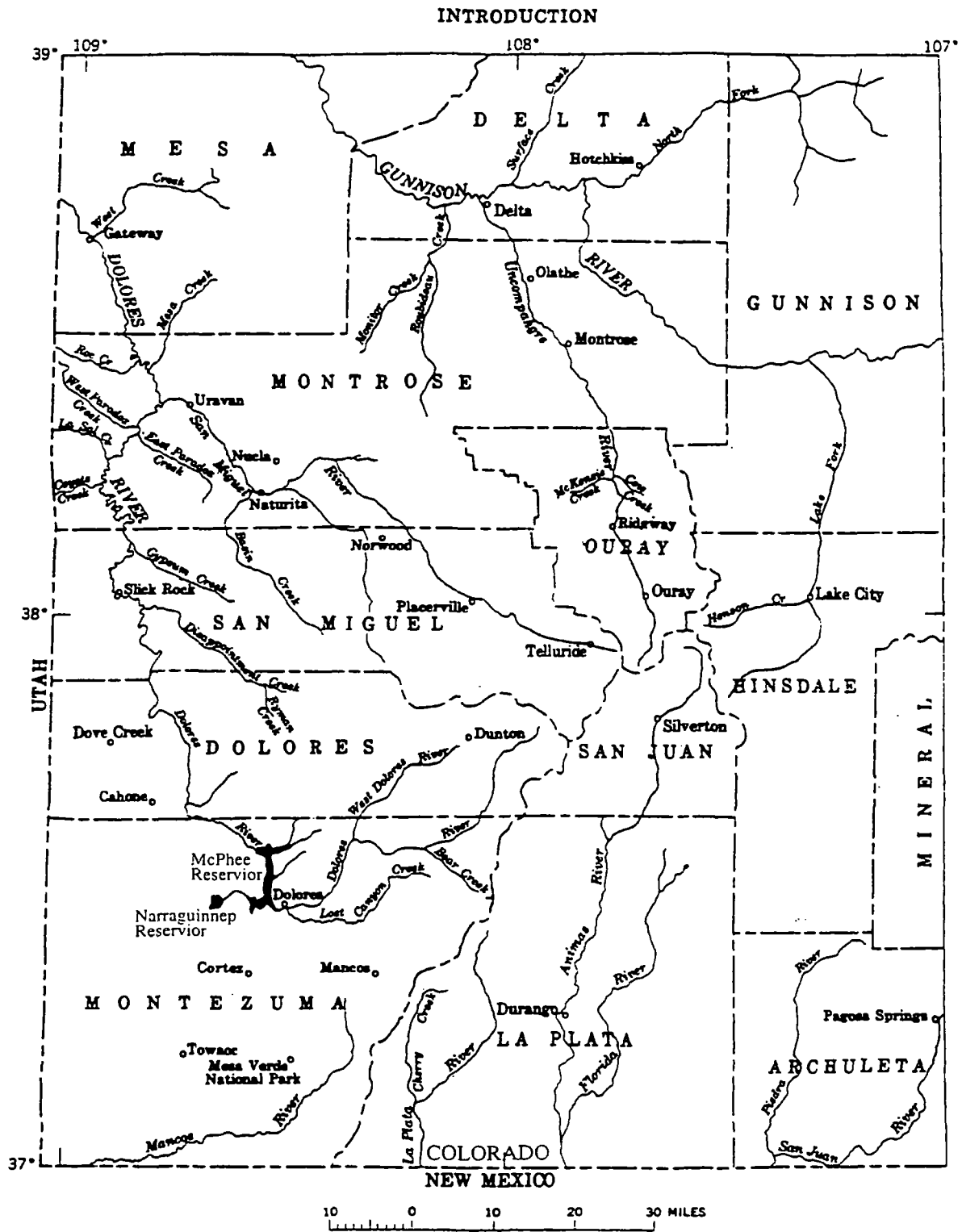


Figure 2. Regional Location map of Dolores River Basin

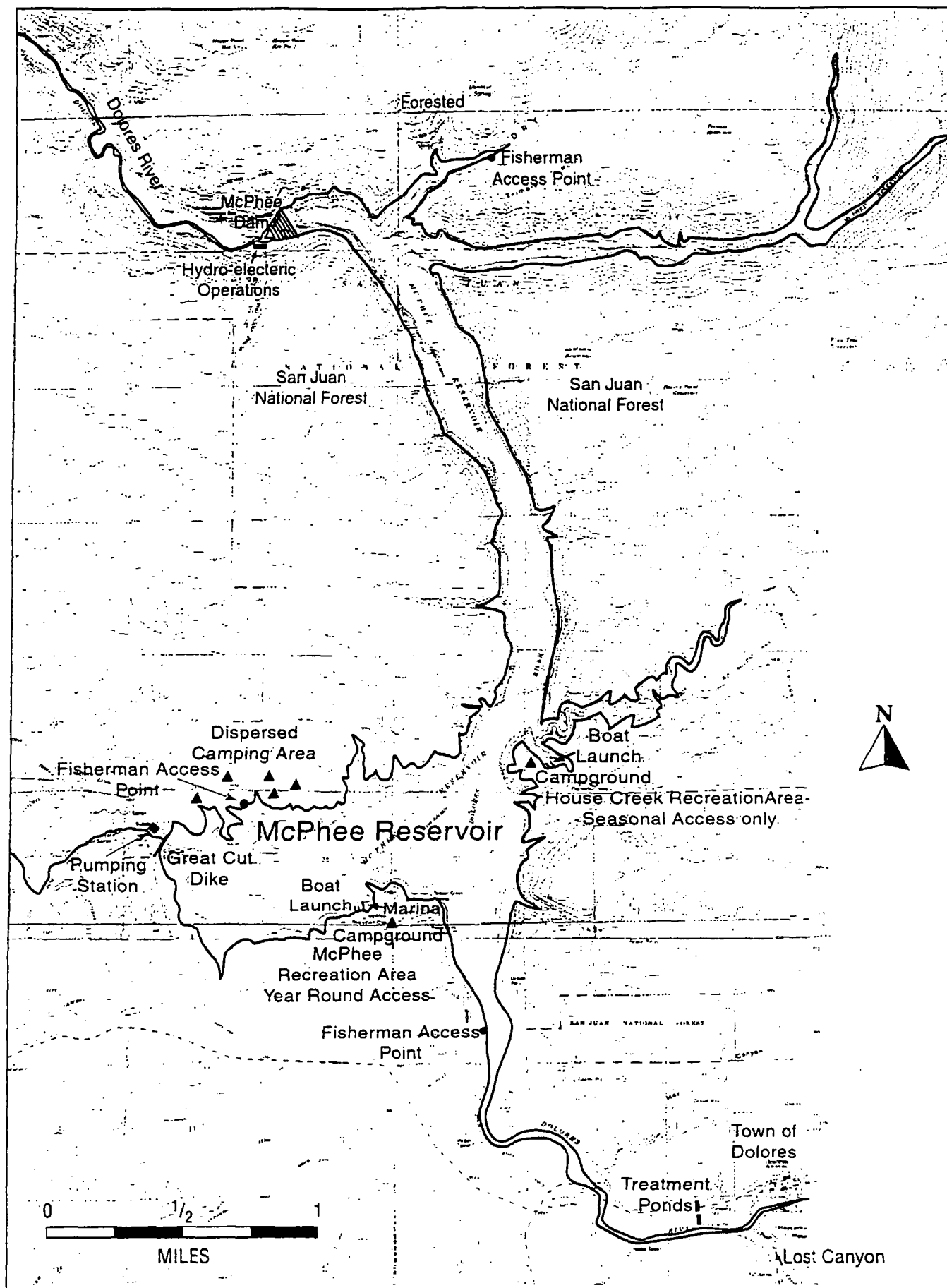


Figure 3a. Map of McPhee Reservoir and vicinity (Watershed shown on separate sampling map)

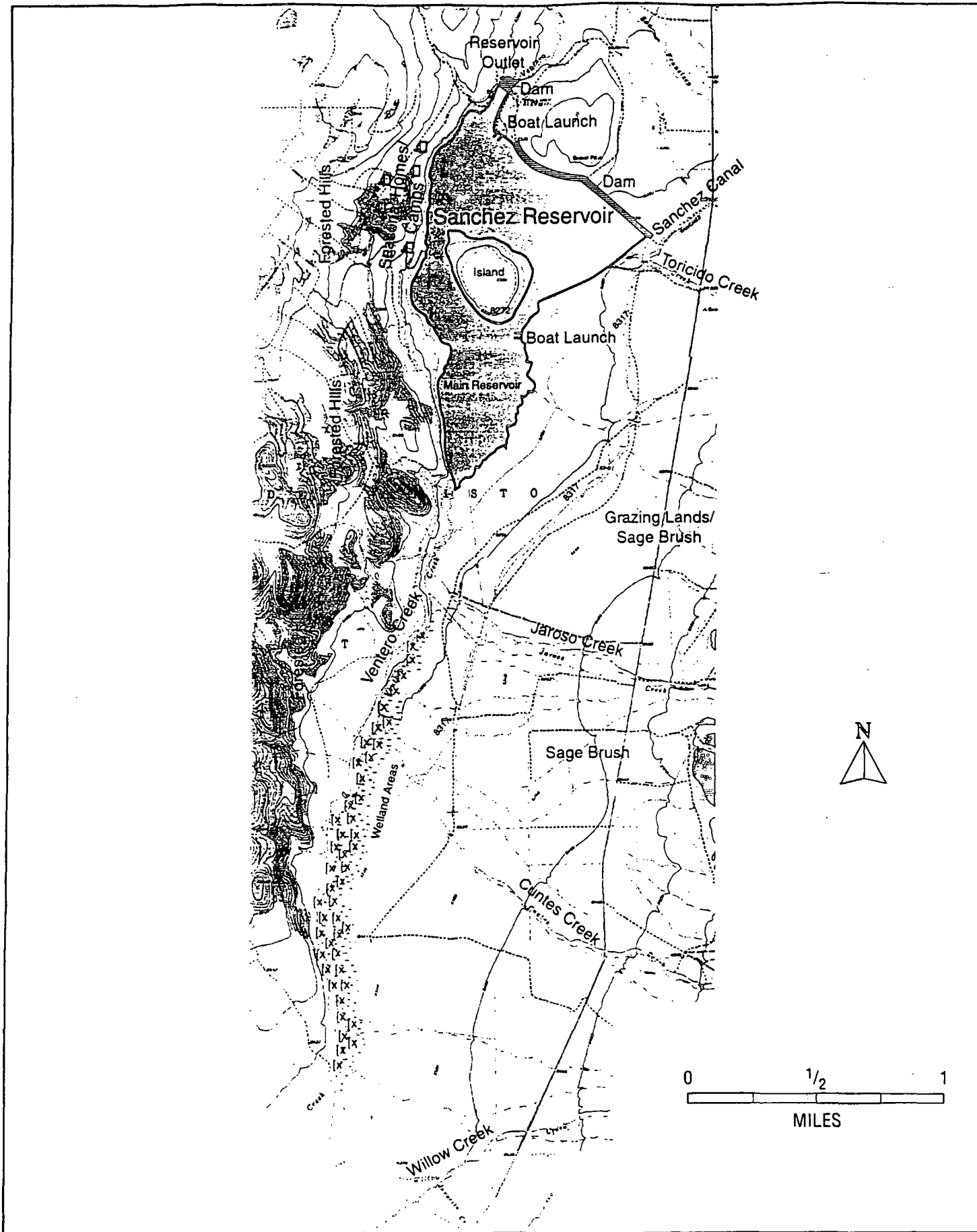


Figure 4. Map of Sanchez Reservoir and vicinity.

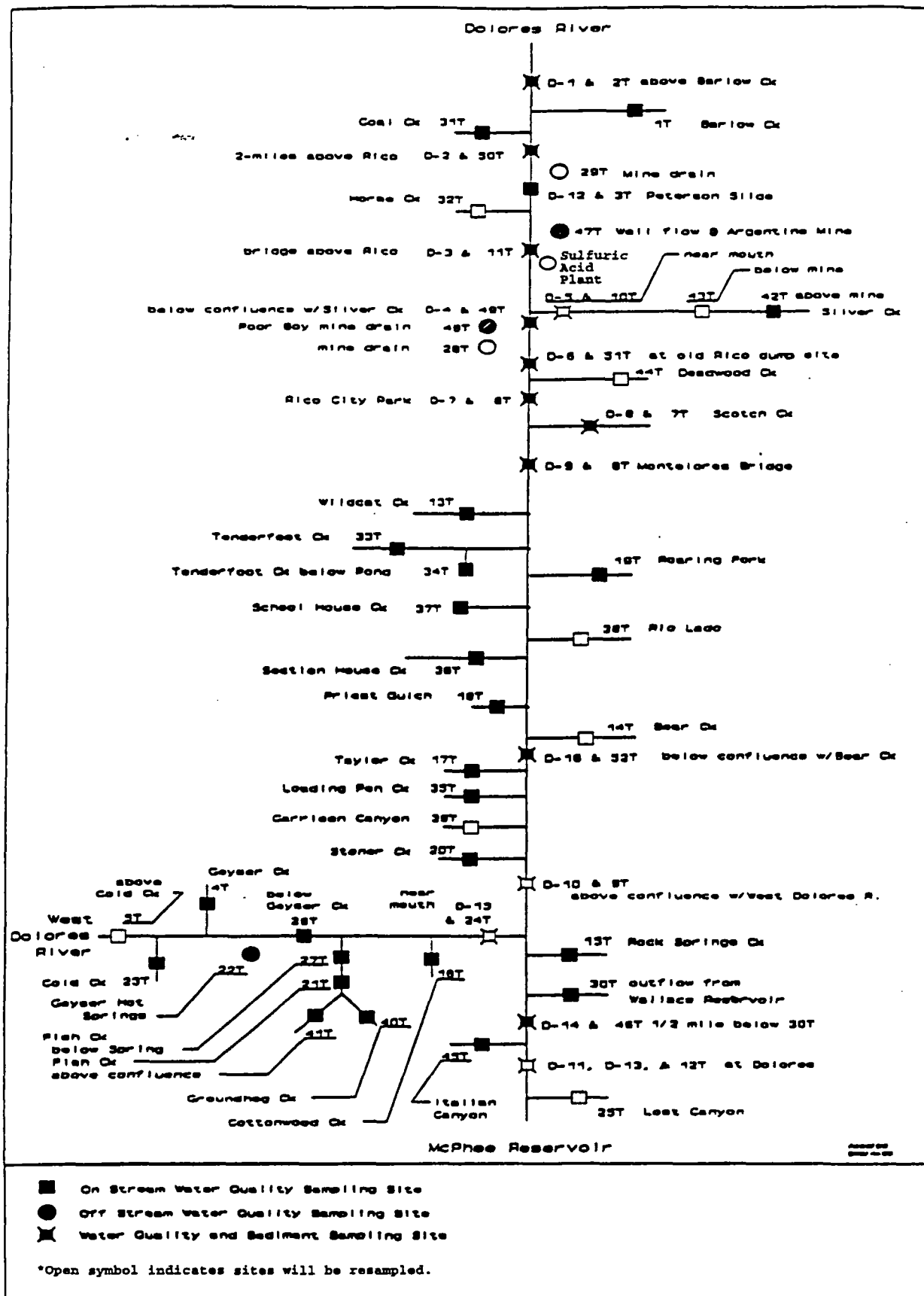


Figure 5. Schematic map of Dolores River Basin sampling site locations (USBR, 1998).

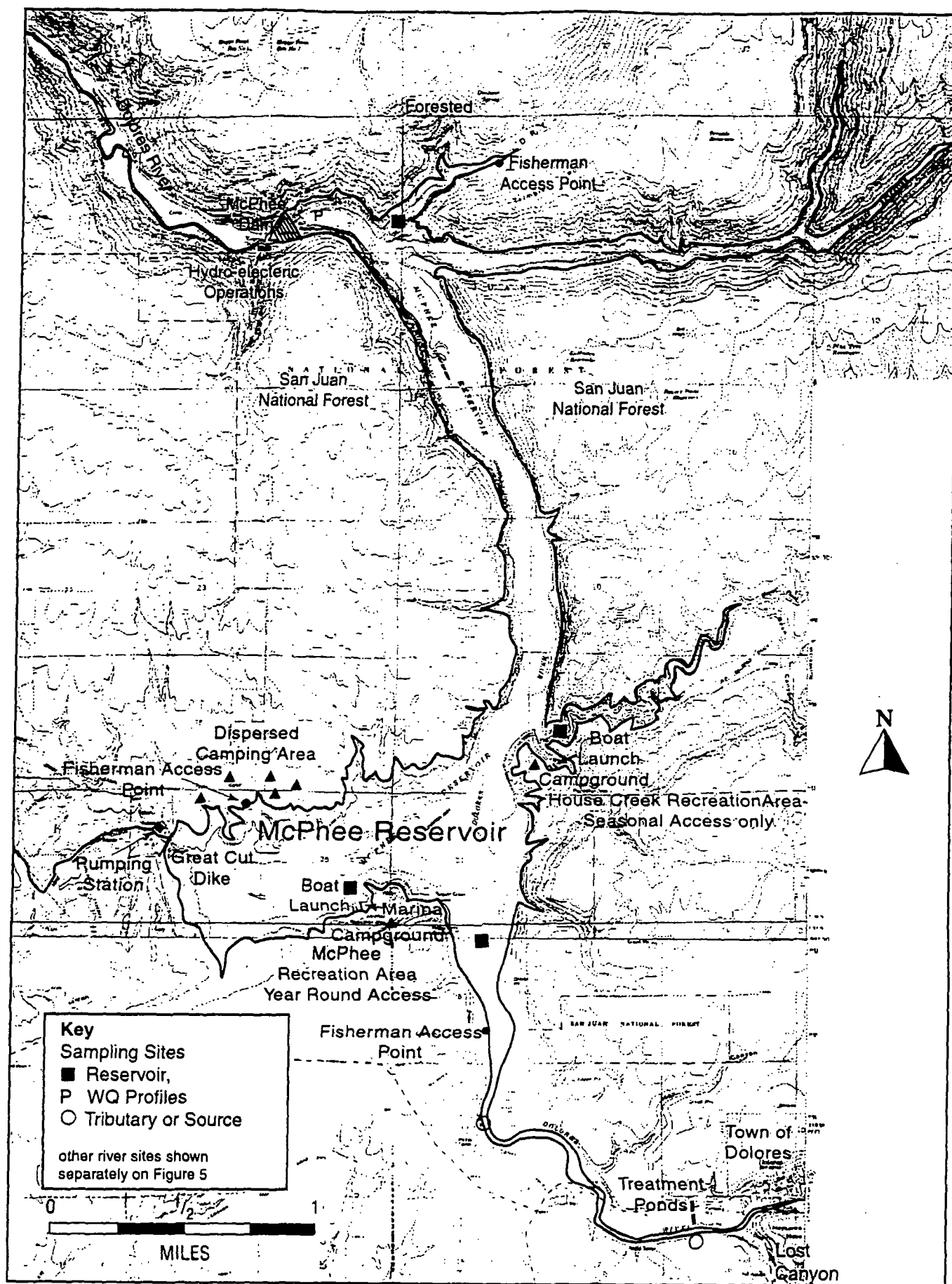


Figure 6. Map of McPhee Reservoir and vicinity

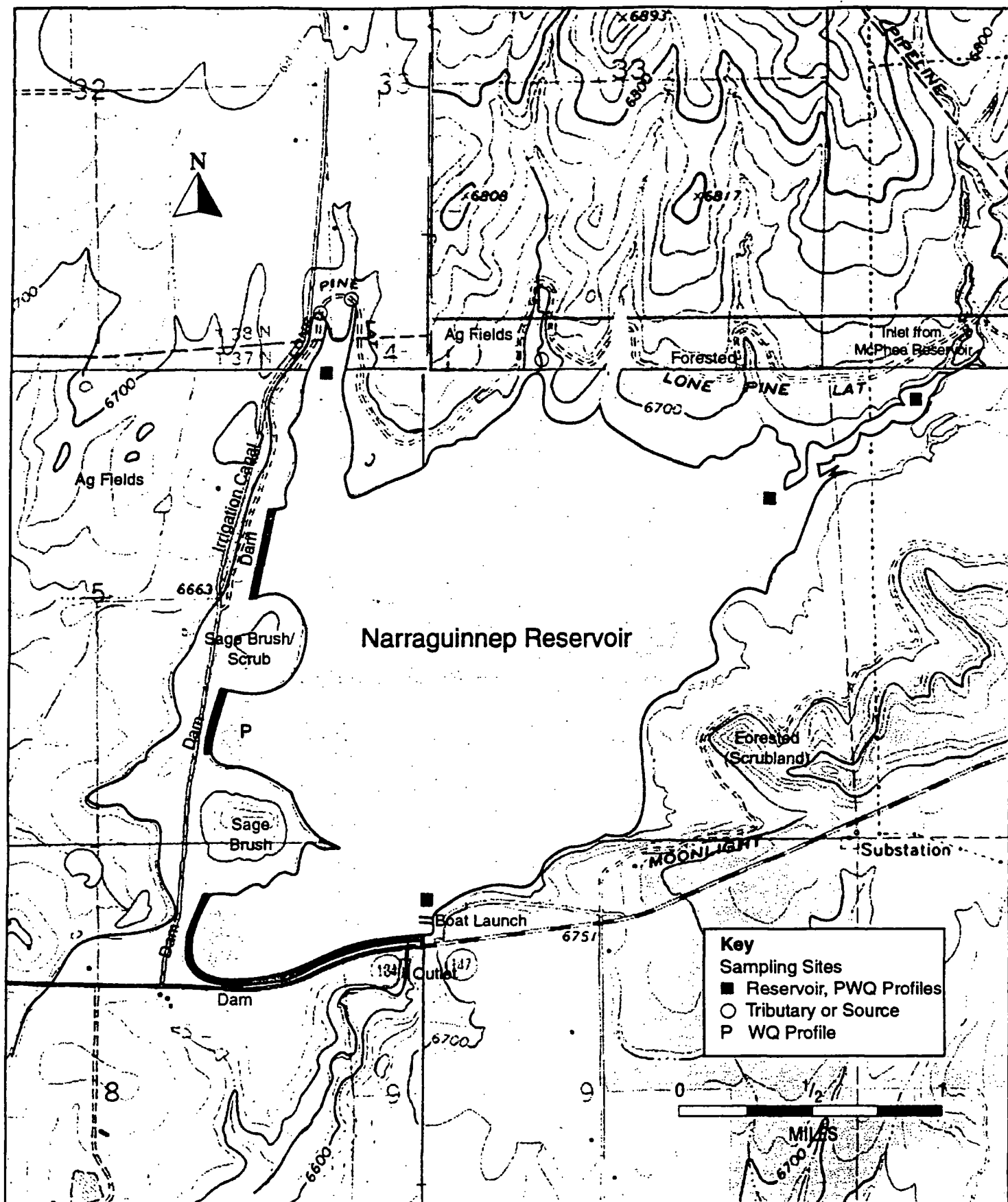


Figure 7. Map of Narraguinnep Reservoir and vicinity.

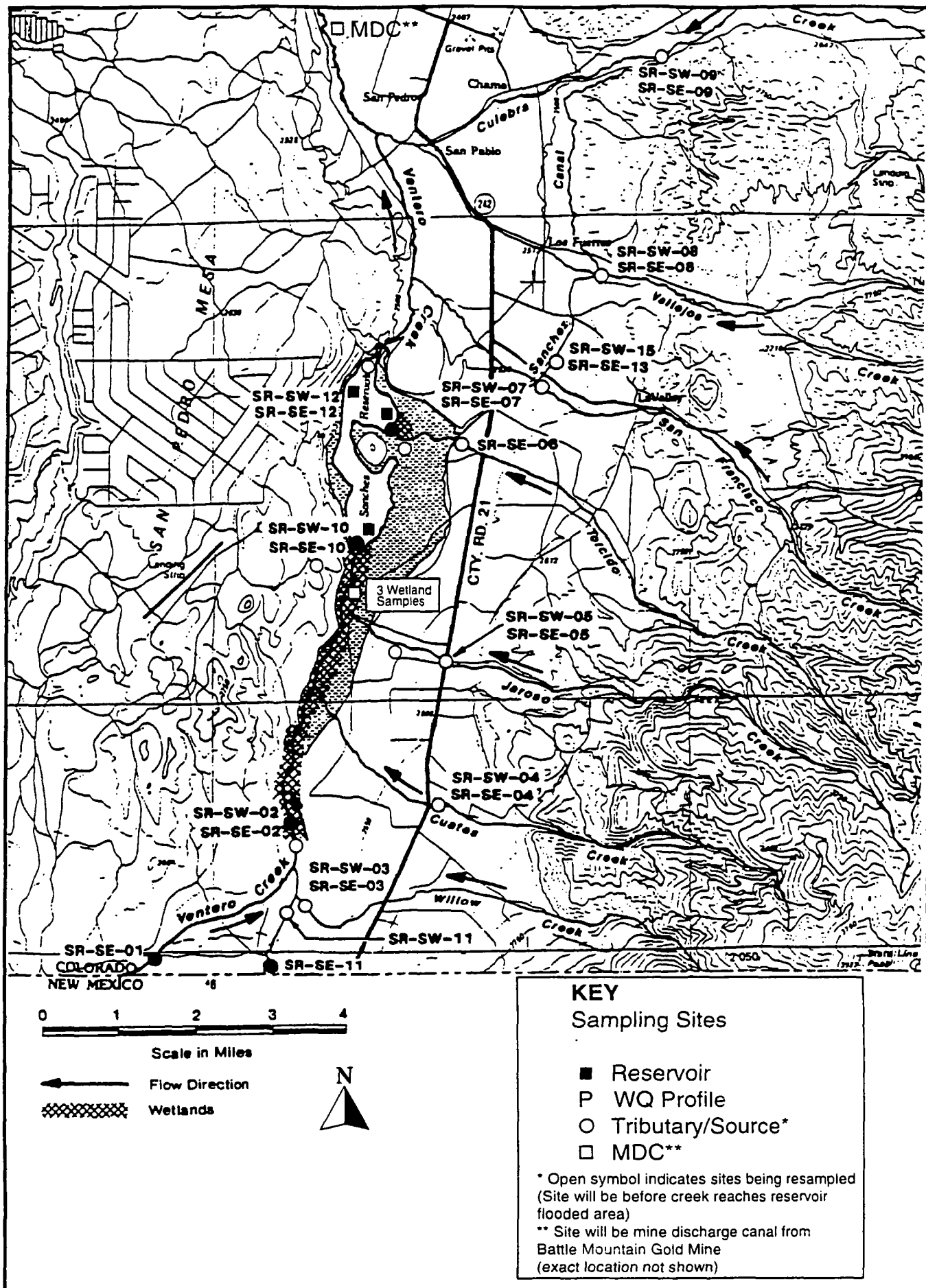


Figure 8. Sanchez Reservoir area with sampling locations.

ATTACHMENT 2

SOP for Ultra-clean Mercury Sampling
SOP for Macroinvertebrate Sampling

Ultra-Clean Aqueous Sample Collection and Preservation (FGS-0008 and EPA Method 1669)

revised January 3, 1995

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1. SCOPE AND APPLICATION

This SOP describes the techniques used to collect and preserve ambient water samples for trace metals, in a way that neither contaminates, loses, or changes the chemical form of the analytes of interest. Samples are collected in the field into previously cleaned and tested samples bottles (FGS-0007) of a material appropriate to the analysis to be conducted.

2. SUMMARY OF METHOD

Sample bottles are cleaned, tested, filled with 0.5% HCl, and double bagged in the laboratory clean-room. At the site the bottle filled with water sample using the "clean -hands - dirty hands" technique. Bottles are sealed tightly and rebagged using the opposite series of steps as were used to open them. Bottles are shipped to the clean-room via over-night courier for further processing (filtration, etc.) and preservation.

3. MATERIALS AND REAGENTS

- 3.1 Sample Bottles. Teflon, glass, or other bottles, as appropriate to the analytes of interest are cleaned and tested according to FGS-0007. Teflon or glass bottles with Teflon caps may be used for all trace metals, while polyethylene and polycarbonate bottles may be used only if mercury is not an analyte of interest.
- 3.2 Sampling Pump. Samples are collected from depth (up to 50 feet) using a battery powered peristaltic pump. A short piece of specially cleaned

silicone silastic tubing is used in the pump head, while all other sampling tubing is 0.25 inch O.D. Teflon, which has been cleaned according to FGS-007. The silastic pump tubing (12 inch sections) are cleaned by heating 24 hours in a sealed Teflon jar with a mixture of 5% acetic acid (reagent grade) + 0.2% HCl (v/v), and then rinsing with DDW and repeating the heating procedure two times with low trace-metal DDW. Pieces of silastic tubing are stored wet in a Teflon jar until use, to avoid contamination by gaseous Hg. NOTES: Any attempt to clean the silastic tubing with strong mineral acids will result in embrittlement. Also

- 3.3 Hydrochloric acid. Trace-metal purified reagent HCl is purchased and pre-analyzed for Hg before use. In general, it is possible to obtain acid containing less than $5 \text{ pg}\cdot\text{mL}^{-1}$ Hg. When a lot number meeting this specification is found, several cases are purchased, and stored in a low Hg atmosphere (i.e.; in clean lab or outside the building). Generally lower values can be obtained in this manner, than by re-distilling acid in the laboratory. So called ULTRA-PURIFIED acids are often the most irreproducibly contaminated (for mercury) grade of acid commercially available and should be avoided.
- 3.4 Nitric acid. Trace-metal purified reagent HNO_3 is purchased and pre-analyzed for Hg and all other metals of interest before use. In general, it is possible to obtain acid containing less than $5 \text{ pg}\cdot\text{mL}^{-1}$ Hg and less than $5 \text{ ng}\cdot\text{mL}^{-1}$ of other trace metals. When a lot number meeting this specification is found, several cases are purchased, and stored in a low Hg atmosphere (i.e.; in clean lab or outside the building). Generally lower values can be obtained in this manner, than by re-distilling acid in the laboratory. So called ULTRA-PURIFIED acids are often the most irreproducibly contaminated (for mercury) grade of acid commercially available and should be avoided, if mercury is an analyte of interest.
- 3.4 0.2N Bromine monochloride. 27 g of KBr are added to a 2.5 L bottle of concentrated HCl analyzed and found to be low in Hg ($<5 \text{ ng}\cdot\text{L}^{-1}$). A clean magnetic stir bar is placed in the bottle, and it is stirred for 1 hour, in a fume hood. Next, 38 g of pre-analyzed, low Hg KBrO_3 are slowly added to the acid with stirring. When all of the KBrO_3 has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. CAUTION: THIS PROCESS GENERATES COPIOUS QUANTITIES OF FREE HALOGENS (Cl_2 , Br, BrCl) WHICH ARE RELEASED FROM THE

BOTTLE. ADD THE KBrO_3 SLOWLY AND IN A WELL OPERATING FUME HOOD!

4. SAMPLE COLLECTION

- 4.1 Samples are collected only into rigorously cleaned Teflon bottles or borosilicate glass bottles with Teflon caps (see FGS-007). Polyethylene or polycarbonate bottles may be used if Hg is not an analyte of interest.
- 4.2 Samples are collected using rigorous ultra-clean protocols which are summarized as follows.
 - 4.2.1 At least two persons, wearing fresh clean-room gloves at all times, are required on a sampling crew.
 - 4.2.2 One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.
 - 4.2.3 The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.
 - 4.2.4 This bottle is opened with a plastic shrouded wrench, and the acidified water is discarded downstream of the sampling site.
 - 4.2.5 The bottle is rinsed once with sample water, and then filled.
 - 4.2.6 Preservative (i.e. 0.5% v/v of high purity HCl for Hg and MMHg , 1.0% v/v HCl for other trace metals) may be added at this time, or within 48 hours at the clean laboratory. Samples collected for Arsenic speciation must be collected into special bottles with a 2 mm hole drilled in the cap, and immediately frozen in liquid nitrogen. NOTE: The hole in the cap is necessary to prevent bottle explosion due to inleakage of liquid nitrogen when the samples are thawed!!
 - 4.2.7 The cap is replaced with the wrench, and the bottle re-bagged in the opposite order from which it was removed.

4.2.8 Clean-room gloves are changed between samples and whenever something not known to be clean is touched.

4.2.9 Water samples are most cleanly obtained by surface grab, using gloved hands, and facing into a flowing body of water or off the bow of a moving boat. If samples are to be taken from depth, the only non-contaminating method generally available is pumping. A peristaltic pump is used with a short (30 cm) piece of FRESHLY cleaned (heating to 70 °C in 2% HCl + 5% CH₃OOH) silicone tubing in the pump. The remainder of the sampling tubing should be 6.5 mm O.D. acid-cleaned Teflon. Once cleaned, silicone tubing quickly absorbs Hg from the air, and so it should be stored in a Teflon jar until use.

4.2.10 CAUTION: DISCRETE SAMPLERS, i.e.; Niskin™ and Kemmerer BOTTLES ARE TO BE AVOIDED, AS, UNDER EVEN THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO CONTAMINATE SAMPLES AT THE ng·L⁻¹ LEVEL. In the event that deep sampling is required, the only discrete sampler which is known to be cleanable is the Teflon-coated, Go-Flo™ (General Oceanics, FL) bottle. These bottles must have all metal components coated with epoxy or silicone, and then be filled and stored for long periods (i.e. 1 month) with 5% HCl, and then tested for contamination by the metal of interest until satisfactory results are obtained.

5. SAMPLE PRESERVATION

5.1 Mercury Samples may be preserved by adding 5 mL·L⁻¹ of concentrated HCl (for both total and methyl Hg analysis) or 5 mL·L⁻¹ BrCl solution, if only total mercury is to be analyzed. Acid and BrCl preserved samples are stable indefinitely (> 6 months), although current EPA mandated holding time is still 28 days. For samples to be analyzed for other metals, using GFAAS, preservation should be with 1.0% HNO₃. In the case that both Hg and other metals are to be analyzed, the following sequence should be employed: (a) pour off c.a. 100 mL into a Teflon bottle, and acidify with 0.5% (v/v) HCl for methyl Hg analysis; (b) Add HNO₃ to the remaining sample to make 1.0% (v/v), shake and allow to stand 1 hour; (c) pour off 100-200 mL into a Teflon bottle, and add 0.2N BrCl to make

1% (v/v) in the aliquot (this sample is for total Hg analysis). The original sample remaining is for GFAAS analysis.

- 5.2 Samples for arsenic speciation must be preserved by quick freezing in liquid nitrogen. For this purpose, use 60-125 mL polyethylene bottles with a 2 mm hole drilled in the cap. The hole is necessary to avoid bottle explosion upon thawing due to rapid evaporation of liquid nitrogen in seepage.
- 5.3 Samples may also be sent back to the laboratory unpreserved if they are 1) collected in teflon bottles, 2) filled to the top with no head space, and 3) sent at 1-4 °C by overnight mail. The samples should be acid preserved soon after arrival at the laboratory (within 48 hours). Samples to be analyzed for dissolved/particulate or volatile Hg speciation must be stored in this manner until analysis of these very labile parameters. Unpreserved samples have been found stable (for Hg speciation) for at least 1 week, when stored in Teflon bottles.
- 5.4 Samples which are acid preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Bloom, 1994). The best approach is to add BrCl directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, these aliquots must be removed prior to the addition of BrCl. If BrCl cannot be added directly to the sample bottle, then it should be vigorously shaken prior to subsampling.
- 5.5 All handling of the samples in the lab should be undertaken in a mercury-free clean air bench, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

6. REFERENCES

- 6.1 Bloom, N.S., Horvat, M., and Watras, C.J. (1995) "Results of the International Mercury Speciation Intercomparison Exercise," *Wat Air Soil Pollut*, (in Press)
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- 6.5 Fitzgerald, W.F. and Watras, C.J. (1989) "Mercury in Surficial Waters of Rural Wisconsin Lakes," *Sci Tot Environ*, 87/88: 223.
- 6.6 Fitzgerald, W.F. and Gill, G.A. (1979) "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis". *Anal. Chem.* 15: 1714.
- 6.7 Bothner, M.H. and Robertson, D.E. (1975) "Mercury Contamination of Sea Water Samples Stored in Polyethylene Containers," *Anal Chem* 47: 592.
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SOP for Benthos Sampling

The sampling techniques described below will collect live animals, some of which may be predatory. Because these samples will be used for analysis of mercury, preservatives should not be used. Animals should be narcotized with club soda and placed on ice while in the field to minimize predation. Samples should be processed immediately upon return from the field to separate the collected invertebrates from any sediment in the sample, and then frozen. Do not freeze the sample before the animals have been completely separated from the sediment, otherwise tissue damage may occur and fluids may be lost. Invertebrate samples should be shipped frozen to the analytical laboratory.

STREAM SAMPLING

The two techniques described below may be used separately, or in combination. The drift net may be set at the tail of the pool, while the Eckman grab is used to sample the sediment further upstream. In this fashion, animals disturbed by the grab sampling activities may be collected in the drift net.

Drift Net

materials:

- drift net
- plastic wash bottle
- waders or hip boots
- sample bottles
- labels
- cooler with ice
- club soda
- aquarium dip net (fine mesh)

procedure:

The drift net collects invertebrates (insects and other mobile animals like amphipods) that have emerged from the sediment or from below rocks and have begun to drift downstream. The drift net should be set in relatively shallow water (< 3 feet) at the tail or head of the pool. Set the net by sliding the two anchor poles through the sides of the net. Place the net in position, and push the poles into the sediment. Ensure that the net will not be pushed over by the current.

The objective is to collect as many invertebrates as possible. Ideal times for setting the net are in the late afternoon to dusk, or in the early morning, as stream invertebrates tend to be most active at these times. The net can be left for any reasonable period of time before recovery. Invertebrates can be "encouraged" to drift by disturbing the sediment, or overturning stones upstream of the net.

The drift net is recovered by pulling the poles from the sediment, and then lifting the mouth of the net to the water surface. The animals will be collected at the end of the net. There should be little sediment in the net. Empty the contents of the net into a labeled sample bottle; if necessary, wash the animals from the net using a minimal amount of water. Add club soda to the sample bottle to narcotize the invertebrates, and place the sample on ice; this will help prevent predation in the sample.

In the laboratory, the club soda should be carefully poured off and the animals separated from any remaining sediment. If a sufficient quantity of animals is obtained, the animals may be sorted into major taxonomic groups. Otherwise, the animals should be kept as a single sample. Blot the excess moisture from the animals using paper towels, and transfer the animals to a sample bottle. Label the bottle and freeze.

Eckman Grab

materials:

- Eckman grab sampler
- extension handle for grab
- waders or hip boots
- 5-gallon bucket(s)
- Nytex mesh sieves: 300 um mesh size [metal sieves must be avoided]
- plastic wash bottle
- sample bottles
- labels
- cooler with ice
- club soda
- aquarium dip net (fine mesh)

procedure:

The grab sampler collects invertebrates that are present in the upper 4 to 6 inches of stream sediment. The Eckman grab is designed to work best in soft sediments composed of fine sand to mud. Because the Eckman grab only covers an area of 6 inches by 6 inches, multiple grab samples may need to be collected to obtain sufficient animals for analysis.

Assemble the grab sampler with the extension handle. Open and lock the jaws of the grab. Be careful not to place hands, fingers, or feet between the open jaws of the grab or injury may result.

Walk out into a pool, and place the sampler vertically on the sediment. Care should be taken while wading, and a route for the return to shore should be decided on before collecting the sample. The sampler may be gently pushed into the top half-inch of sediment. Do not push too deeply, or the grab will not operate properly. Trigger the

release mechanism on the grab. Lift the grab vertically out of the sediment and carry the grab to shore.

Open the jaws of the grab over the 5-gallon bucket, and empty the sediment into the bucket. Depending on the size of the sieve, place a portion of the sediment in the sieve. Gently shake the sieve using an up-and-down, or side-to-side, motion while the bottom of the sieve is in the water. This technique will float the animals, while allowing the sediment to pass through the sieve. Be careful not to wash animals over the top of the sieve. The amount of sediment that will pass through the sieve is dependent on the sediment grain size, and the amount of sediment initially placed on the sieve.

Transfer the remaining sediment and animals on the sieve to a labeled sample bottle using a minimum amount of water. Continue until all the material in the 5-gallon bucket has been sieved, or sufficient animals have been collected. Add club soda to the sample bottle to narcotize the invertebrates, and place the sample on ice; this will help prevent predation in the sample.

In the field laboratory, the club soda should be carefully poured off and the animals separated from any remaining sediment. If only a small amount of sediment is present, the animals may be picked out and transferred to a sample bottle using non-metallic forceps. If a quantity of sediment is present, the larger, easily visible, animals can be removed using non-metallic forceps.

The animals should be removed from the remaining sediment using an elutriation technique. Transfer the sediment to a three to five liter bucket. Add cold water to the bucket to approximately three times the volume of the sediment. Stir the sediment. Swirl the bucket to lift the animals from the sediment and pour the water through a fine-mesh aquarium dip net. Because the animals are still alive, they may try to swim down to the bottom of the bucket; rapid swirling and pouring will minimize this. Some sediment may be elutriated with the animals, this is normal. Three to five rinses per batch of sediment are generally required.

If a sufficient quantity of animals is obtained, the animals may be sorted into major taxonomic groups. Otherwise, the animals should be kept as a single sample. Blot the excess moisture from the animals using paper towels, and transfer the animals to a sample bottle. Label the bottle and freeze.

RESERVOIR SAMPLING

Reservoir sampling will be conducted using a grab sampler. The grab sampler may be either a petite Ponar grab or the Eckman grab. Sampling is limited to waters less than 100 feet deep using either of these grabs.

materials:

Petite Ponar [or Eckman grab] sampler

rope
flat-bottom boat
5-gallon bucket(s)
Nytex mesh sieves: 300 um mesh size [metal sieves must be avoided]
plastic wash bottle
sample bottles
labels
cooler with ice
club soda
aquarium dip net (fine mesh)

procedure:

The petite Ponar grab sampler collects invertebrates that are present in the upper 1 to 2 inches of lake sediment, whereas the Eckman grab can collect samples to 4 to 6 inches depth. Both grabs are designed to work best in soft sediments composed of fine sand to mud. The petite Ponar grab may be used in slightly coarser sediments than the Eckman. The Eckman grab must be triggered while it is vertical, and may therefore be limited to shallower water than the Ponar. Because the grabs only cover a relatively small area, multiple grab samples may need to be collected to obtain sufficient animals for analysis.

The following discussion will describe deployment of the petite Ponar grab with limited discussion of the Eckman grab.

Assemble the Ponar sampler, open and lock the jaws of the grab. Be careful not to place hands, fingers, or feet between the open jaws of the grab or injury may result.

[The Eckman sampler is assembled by sliding the messenger onto the rope, and then feeding the rope through the yoke of the sampler and knotting the rope.]

Lower the sampler over the side of the boat being careful to maintain tension on the line to prevent the jaws of the grab from closing. When the Ponar grab reaches the bottom, release the tension on the rope, thus releasing the hook holding the jaws open. Apply tension to the rope in a smooth manner, closing the jaws and lifting the grab from the bottom. Haul the grab to the surface.

[If the Eckman grab is used, tension should be maintained on the rope when the grab reaches the bottom. Care should be taken to minimize any rocking of the boat, as this will lift the grab off the bottom. The grab is triggered by allowing the messenger to slide down the rope to the grab. Once the grab has been triggered, it may be hauled to the surface.]

Open the jaws of the grab over the 5-gallon bucket, and empty the sediment into the bucket. Depending on the size of the sieve, place a portion of the sediment in the sieve. Gently shake the sieve using an up-and-down, or side-to-side, motion while the bottom of the sieve is in the water. This technique will float the animals, while allowing the

sediment to pass through the sieve. Be careful not to wash animals over the top of the sieve. The amount of sediment that will pass through the sieve is dependent on the sediment grain size, and the amount of sediment initially placed on the sieve.

Transfer the remaining sediment and animals on the sieve to a labeled sample bottle using a minimum amount of water. Continue until all the material in the 5-gallon bucket has been sieved, or sufficient animals have been collected. Add club soda to the sample bottle to narcotize the invertebrates, and place the sample on ice; this will help prevent predation in the sample.

In the field laboratory, the club soda should be carefully poured off and the animals separated from any remaining sediment. If only a small amount of sediment is present, the animals may be picked out and transferred to a sample bottle using non-metallic forceps. If a quantity of sediment is present, the larger, easily visible, animals can be removed using non-metallic forceps.

The animals should be removed from the remaining sediment using an elutriation technique. Transfer the sediment to a three to five liter bucket. Add cold water to the bucket to approximately three times the volume of the sediment. Stir the sediment. Swirl the bucket to lift the animals from the sediment and pour the water through a fine-mesh aquarium dip net. Because the animals are still alive, they may try to swim down to the bottom of the bucket; rapid swirling and pouring will minimize this. Some sediment may be elutriated with the animals, this is normal. Three to five rinses per batch of sediment are generally required.

If a sufficient quantity of animals is obtained, the animals may be sorted into major taxonomic groups. Otherwise, the animals should be kept as a single sample. Blot the excess moisture from the animals using paper towels, and transfer the animals to a sample bottle. Label the bottle and freeze.

Method 1669

**Sampling Ambient Water for Trace Metals at EPA Water Quality
Criteria Levels**

July 1996

**U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460**

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This version of the method was prepared after observations of sampling teams from the University of California at Santa Cruz, the Wisconsin Department of Natural Resources, the U.S. Geological Survey, and Battelle Ocean Sciences. The assistance of personnel demonstrating the sampling techniques used by these institutions is gratefully acknowledged.

Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Further Information

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Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489-8190

Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

- 1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.
- 1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr ⁺³	16065-83-1
Chromium (VI)	Cr ⁺⁶	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

- 1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.
- 1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 CFR Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.
- 1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

- 1.6 Clean and Ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques (Reference 10).
- 1.7 This sampling method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 11).
- 1.8 Method 1669 is "performance-based"; i.e., an alternate sampling procedure or technique may be used, so long as neither samples nor blanks are contaminated when following the alternate procedures. Because the only way to measure the performance of the alternate procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 9.2 provides additional details on the tests and documentation required to support equivalent performance.
- 1.9 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.
- 1.10 The procedures in this method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 Summary of Method

- 2.1 Before samples are collected, all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory or cleaning facility is responsible for generating an acceptable equipment blank to demonstrate that the sampling equipment and containers are free from trace metals contamination before they are shipped to the field sampling team. An acceptable blank is one that is free from contamination below the minimum level (ML) specified in the referenced analytical method (Section 9.3).
- 2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

NOTE: EPA has found that, in some cases, it may be possible to empty the weak acid solution from the bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

- 2.3 The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water (Section 7.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination

of trivalent chromium, the sampling team processes additional QC aliquots are processed as described in Section 9.6.

- 2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.
- 2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.
- 2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.
- 2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.
- 2.8 Sampling
 - 2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.
 - 2.8.2 Samples may be collected while working from a boat or while on land.
 - 2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.
 - 2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.
- 2.9 Samples for dissolved metals are filtered through a 0.45 μm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.
- 2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.
- 2.11 Sampling activities must be documented through paper or computerized sample tracking systems.

3.0 Definitions

- 3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.
- 3.2 Definitions of other terms are given in the Glossary (Section 15.0) at the end of this method.

4.0 Contamination and Interferences

4.1 Contamination Problems in Trace Metals Analysis

- 4.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 12). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.
- 4.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.2 Contamination Control

- 4.2.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.
 - 4.2.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.
 - 4.2.1.2 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements. Requirements and suggestions for protecting the Apparatus are given in this sampling method and in the methods referenced in Table 1.
 - 4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting either in contamination or low-biased results (Reference 3). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

4.2.2.3.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in

contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 13).

4.2.2.3.3 **Serialization**—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.

4.2.2.3.4 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.2.2.3.5 Details for recleaning the Apparatus between collection of individual samples are provided in Section 10.0.

4.2.2.4 **Avoid sources of contamination**—Avoid contamination by being aware of potential sources and routes of contamination.

4.2.2.4.1 **Contamination by carryover**—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).

4.2.2.4.2 **Contamination by samples**—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of

metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.

4.2.2.4.3 Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling. It is also suggested that the organization responsible perform personal hygiene monitoring of each sampling team member who uses this method and that the results of this monitoring be made available to the member.
- 5.2 Operating in and around waterbodies carries the inherent risk of drowning. Life jackets must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.
- 5.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

6.0 Apparatus and Materials

NOTE: Brand names, suppliers, and part numbers are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.

- 6.1 All sampling equipment and sample containers must be precleaned in a laboratory or cleaning facility, as described in the methods referenced in Table 1, before they are shipped to the field site. Performance criteria for equipment cleaning is described in the referenced methods. To minimize difficulties in sampling, the equipment should be packaged and arranged to minimize field preparation.
- 6.2 Materials such as gloves (Section 6.7), storage bags (Section 6.8), and plastic wrap (Section 6.9), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.
- 6.3 Sample Bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. If mercury is a target analyte, fluoropolymer or glass bottles should be used. Refer to the methods referenced in Table 1 for bottle cleaning procedures.
 - 6.3.1 Cleaned sample bottles should be filled with 0.1% HCl (v/v). In some cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).
 - 6.3.2 Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. Preparation of the devices in the field should be done within the glove bag (Section 6.6). Regardless of design, sampling devices must be constructed of nonmetallic material (Section 4.2.2.3.1) and free from material that contains metals. Fluoropolymer or other material shown not to adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.
- 6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.
 - 6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

- 6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.
 - 6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.
 - 6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).
- 6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.
 - 6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.
 - 6.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, Section 6.15) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 14). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.
 - 6.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.
 - 6.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (Reference 14).

6.5.2 Continuous-flow sampler (References 16-17)—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

6.5.2.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

6.5.2.2 The sampling team assembles the system in the field as described in Section 8.2.8. System components include an optional polyethylene pole to remove sampling personnel from the immediate vicinity of the sampling point and the pump, tubing, filter, and filter holder listed in Sections 6.14 and 6.15.

6.6 Field-Portable Glove Bag—I2R, Model R-37-37H (nontalc), or equivalent. Alternately, a portable glove box may be constructed with a nonmetallic (PVC pipe or other suitable material) frame and a frame cover made of an inexpensive, disposable, nonmetallic material (e.g., a thin-walled polyethylene bag) (Reference 7).

6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.

6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.

6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.

6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).

6.9 Plastic Wrap—Clean, colorless polyethylene.

6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.

6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.

6.12 Wind Suit—Pamida, or equivalent.

NOTE: This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.

6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.

6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all

traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.

6.13 Boat

6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.

6.13.1.2 Samples should be collected upstream of boat movement.

6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:

6.13.2.1 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement.

6.13.2.2 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution.

6.13.2.3 The boat should be frequently visually inspected for possible contamination.

6.13.2.4 After sampling, the boat should be returned to the laboratory or cleaning facility, cleaned as necessary, and stored away from any sources of contamination until next use.

6.14 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.

6.14.1 Filter—0.45 μm , 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175, or equivalent.

- 6.14.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps.

NOTE: A filter holder may not be required if one or a few samples are to be collected. For these cases, it may only be necessary to attach the filter to the outlet of the tubing connected to the pump.

- 6.15 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

NOTE: Equivalent pumps may include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.

- 6.15.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

- 6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

- 6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

- 6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

- 6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

- 6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.

- 6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.

- 6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).
- 6.17.2 Filters—0.4 μm , 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).
- 6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.
- 6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 μL)
- 6.17.5 Wrist-action shaker—Burrel or equivalent.
- 6.17.6 Fluoropolymer wash bottles—One filled with reagent water (Section 7.1) and one filled with high-purity 10% HCl (Section 7.4.4), for use in rinsing forceps and pipet tips.

7.0 Reagents and Standards

- 7.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.
- 7.2 Nitric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.
- 7.3 Sodium Hydroxide—Concentrated, 50% solution for use when field-preserving samples for hexavalent chromium determinations (Section 8.4.5).
- 7.4 Reagents—For field-processing aliquots for trivalent chromium determinations
 - 7.4.1 Nitric Acid, Ultrapure—For use when field-preserving samples for trivalent chromium determinations (Sections 6.17 and 8.4.4).
 - 7.4.2 Ammonium Iron (II) Sulfate Solution (0.01M)—Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.
 - 7.4.3 Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by

adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.

- 7.4.4 Hydrochloric acid—High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.
- 7.4.5 Chromium stock standard solution (1000 µg/mL)—Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.
- 7.4.6 Standard chromium spike solution (1000 µg/L)—Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.
- 7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

- 8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.
- 8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).
- 8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).

- 8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.
- 8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume should be collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.
- 8.2.1 Four sampling procedures are described:
- 8.2.1.1 Section 8.2.5 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.
 - 8.2.1.2 Section 8.2.6 describes a procedure for using a grab sampling device to collect samples.
 - 8.2.1.3 Section 8.2.7 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.
 - 8.2.1.4 Section 8.2.8 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.
- 8.2.2 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the bow.
- If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.
- 8.2.3 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

- 8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.
- 8.2.5 Manual collection of surface samples directly into the sample bottle.
 - 8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).
 - 8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
 - 8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.
 - 8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.
 - 8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.
 - 8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.
 - 8.2.5.7 "Dirty hands" zips the outer bag.

8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.5.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 8.3.

8.2.6 Sample collection with grab sampling device—The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 6.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 6.4.2.

8.2.6.1 The sampling team puts on gloves (and wind suits, if applicable). Ideally, a sample bottle will have been preattached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation, described in Section 6.4.2, inside the field-portable glove bag (Section 6.6).

8.2.6.2 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

8.2.6.3 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

8.2.6.4 "Clean hands" changes gloves.

8.2.6.5 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.

8.2.6.6 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.

8.2.6.7 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 8.2.5.6 through 8.2.5.7.

8.2.6.8 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 7.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

8.2.6.9 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.

8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)

8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).

8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.

8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).

8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.

8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.

8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.

8.2.7.8 Both "clean hands" and "dirty hands" change gloves.

8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.

8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.

8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."

8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.

8.2.7.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.8 Continuous-flow sampling (Figure 4 and Section 6.5.2)—The continuous-flow sampling system uses peristaltic pump (Section 6.15) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.

8.2.8.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump (Section 6.15), SEBS-resin tubing (Section 6.15.2), batteries (Section 6.15.4), gloves (Section 6.7), plastic wrap (Section 6.9), wind suits (Section 6.12), and, if samples are to be filtered, the filtration apparatus (Section 6.14) from the coolers or storage containers in which they are packed.

8.2.8.2 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 6.7.2).

8.2.8.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.

8.2.8.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.

8.2.8.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 6.7.1).

8.2.8.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.

8.2.8.7 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

NOTE: The filtration apparatus is not attached until immediately before sampling to prevent buildup of particulates from clogging the filter.

8.2.8.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.

8.2.8.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.3 Sample Filtration—The filtration procedure described below is used for samples collected using the manual (Section 8.2.5), grab (Section 8.2.6), or jar (Section 8.2.7) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 8.2.8.7. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

- 8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
- 8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.
- 8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.
- 8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
- 8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.
- 8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).
- 8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."
- 8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

- 8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.
- 8.4.2 If field preservation is required, preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus (Section 6.17.3), and an area should be available for setting up the wrist-action shaker (Section 6.17.5). It is also advisable to set up a work area that contains a "clean" cooler for storage of clean equipment, a "dirty" cooler for storage of "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.

- 8.4.3 Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.
- 8.4.4 Preservation of aliquots for trivalent chromium (References 8-9).
- 8.4.4.1 Decant 100 mL of the sample into a clean polyethylene bottle.
- 8.4.4.2 Clean an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution (Section 7.4.3) to each sample and blank.
- 8.4.4.3 Cap each bottle tightly, place in a clean polyethylene bag, and shake on a wrist action shaker (Section 6.17.5) for one hour.
- 8.4.4.4 Vacuum-filter the precipitate through a 0.4 μ m pretreated filter membrane (Section 6.17.2), using fluoropolymer forceps (Section 6.17.1) to handle the membrane, and a 47 mm vacuum filtration apparatus with a precleaned filter holder (Section 6.17.3). After all sample has filtered, rinse the inside of the filter holder with approximately 15 mL of reagent water.
- 8.4.4.5 Using the fluoropolymer forceps, fold the membrane in half and then in quarters, taking care to avoid touching the side containing the filtrate to any surface. (Folding is done while the membrane is sitting on the filter holder and allows easy placement of the membrane into the sample vial). Transfer the filter to a 30 mL fluoropolymer vial. If the fluoropolymer vial was not pre-equipped with the ultrapure nitric acid (Section 7.4.1), rinse the pipet by drawing and discharging 1 mL of 10% HCl followed by 1 mL of reagent water into a waste container, and add 1 mL of ultrapure nitric acid to the sample vial.
- 8.4.4.6 Cap the vial and double-bag it for shipment to the laboratory.
- 8.4.4.7 Repeat Steps 8.4.4.4-8.4.4.6 for each sample, rinsing the fluoropolymer forceps and the pipet with 10% high-purity HCl followed by reagent water between samples.
- 8.4.5 Preservation of aliquots for hexavalent chromium (Reference 20).
- 8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.
- 8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.
- 8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require sampling personnel to collect a clean equipment blank before performing on-site field activities.

9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.

9.3.5 The equipment blank must be analyzed using the procedures detailed in the referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

9.4 Field Blank

9.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for

every 10 samples that are collected at a given site. Field blanks are collected before sample collection.

- 9.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.
 - 9.4.3 Filter the field blanks using the procedures described in Section 8.3.
 - 9.4.4 If it is necessary to acid clean the sampling equipment between samples (Section 10.0), a field blank should be collected after the cleaning procedures but before the next sample is collected.
 - 9.4.5 If trivalent chromium aliquots are processed, a separate field blank must be collected and processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.
- 9.5 Field Duplicate
- 9.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.
 - 9.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.
 - 9.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 8.3. Field duplicates for trivalent chromium must be processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.
- 9.6 Additional QC for Collection of Trivalent Chromium Aliquots
- 9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 μm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.
 - 9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 μm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

- 9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.

9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 µg/L.

9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

- 10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples is unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.

- 10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.

- 10.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:

10.3.1 In the glove bag, and using the "clean hands/dirty hands" procedure in Section 8.2.5, process the dilute nitric acid solution (Section 7.2) through the Apparatus.

10.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.

10.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.

10.3.4 Collect a field blank as described in Section 9.4.

10.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.

- 10.4 Procedures for recleaning trivalent chromium preservation equipment between samples are described in Section 8.4.4.

11.0 Method Performance

Samples were collected in the Great Lakes during September–October 1994 using the procedures in this sampling method.

12.0 Pollution Prevention

- 12.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.
- 12.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.
- 12.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

13.0 Waste Management

- 13.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.
- 13.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

14.0 References

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15.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

- 15.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.
- 15.2 **Apparatus**—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.
- 15.3 **Equipment Blank**—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.
- 15.4 **Field Blank**—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine whether the field or sample transporting procedures and environments have contaminated the sample.
- 15.5 **Field Duplicates (FD1 and FD2)**—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.
- 15.6 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
- 15.7 **May**—This action, activity, or procedural step is optional.
- 15.8 **May Not**—This action, activity, or procedural step is prohibited.
- 15.9 **Minimum Level (ML)**—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).
- 15.10 **Must**—This action, activity, or procedural step is required.
- 15.11 **Reagent Water**—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.

- 15.12 Should—This action, activity, or procedural step is suggested but not required.
- 15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

**TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS
APPLICABLE TO METHOD 1669**

Method	Technique	Metal	MDL (µg/L) ¹	ML (µg/L) ²
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Trivalent Chromium	0.1	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS	Cadmium	0.0024	0.01
		Copper	0.024	0.1
		Lead	0.0081	0.02
		Nickel	0.029	0.1

¹ Method Detection Limit as determined by 40 CFR Part 136, Appendix B.

² Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels, March 22, 1994.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% HNO_3 to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 μm membrane, add 1 mL 10% HNO_3 ; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH ; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to $\text{pH} < 2$; Total & Methyl: Add 0.5% high-purity HCl ; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps